Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Facile Synthesis of 9*H*-Pyrrolo[1,2-α]indoles Via Brønsted Acid Catalyzed Cascade Reaction

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Table of Contents

1. General information……S3

2. General procedure for the synthesis of 9*H*-pyrrolo[1,2-α]indoles……S4

3. Control experiments……S21

4. Intermediate characterization……S22

5. References……S23

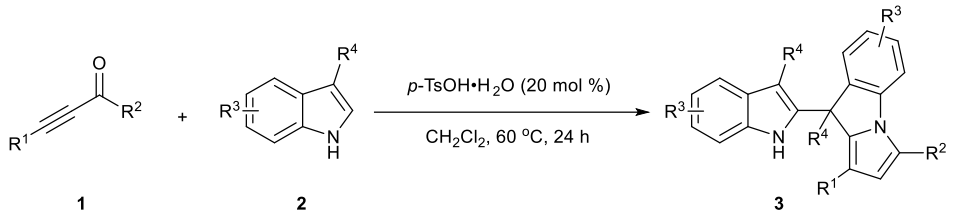
6. Crystal data of **3aa** ……S24

7. NMR spectrum……S26

1. General information

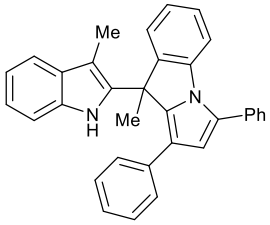
Catalytic reactions were carried out in sealed tubes under an air atmosphere with dry dichloromethane. All the ynone **1** and indole **2** have been synthesized following procedures reported in the literature.[1,2] Other chemicals were obtained from commercial sources and were used without further purification. The ^{1}H and ^{13}C NMR spectra were recorded on JEOL at 400 MHz for ^{1}H or at 100 MHz for ^{13}C, respectively. The chemical shifts (δ) for ^{1}H and ^{13}C are given in ppm relative to residual signals of the solvents ($CHCl_3$ 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR). Mass spectra and high-resolution mass spectra were measured on a Thermo-DFS mass spectrometer. Analysis of crude reaction mixture was done on an Agilent 7890 GC System with an Agilent 5975 Mass Selective Detector. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used, Silica gel 60H (200-300 mesh) manufactured by Qingdao Haiyang Chemical Group Co. (China) were used for general chromatography, using UV light as the visualizing agent and an acidic mixture of ceric ammonium molybdate or basic aqueous potassium permangante ($KMnO_4$), and heat as developing agents. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator.

2. General procedure for the synthesis of 9*H*-pyrrolo[1,2-α]indoles



1 2 3

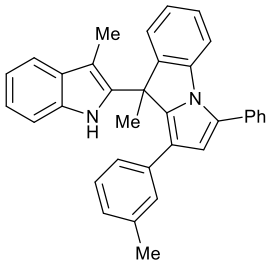
A solution of *p*-TsOH ·H_2O (7.6 mg, 0.04 mmol, 20 mol%), ynone **1** (0.2 mmol) and 3-substituted indole **2** (0.8 mmol) in CH_2Cl_2 (0.4 mL) was stirred at 60 °C for 24 h. After cooling to ambient temperature, the mixture was purified by column chromatography (Petroleum Ether /EtOAc) to afford the desired product **3**.



9-methyl-9-(3-methyl-1*H*-indol-2-yl)-1,3-diphenyl-9*H*-pyrrolo[1,2-α]indole (3aa)

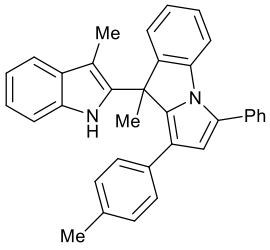
The general procedure was followed using substrate ynone **1a** and indole **2a** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 100:1) yielded **3aa** (66 mg, 74%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.70 (d, J = 8.0 Hz, 2H), 7.55 – 7.51 (m, 3H), 7.46 (t, J = 6.8 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.23 – 7.10 (m, 10H), 7.01 (t, J = 7.2 Hz, 1H), 6.62 (s, 1H), 2.08 (s, 3H), 2.05 (s, 3H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3, 139.7, 138.9, 135.3, 135.2, 134.7, 132.7, 130.5, 129.3, 129.0, 128.64, 128.61, 127.9, 127.7, 127.0, 125.8, 124.4, 124.2, 121.7, 119.9, 119.3, 118.5, 114.1, 112.0, 110.7, 108.2, 45.6, 22.9, 8.8 ppm. HR-MS (ESI): *m/z* calcd for $C_{33}H_{26}N_2$ $[M+H]^+$ 451.21742, found: 451.21625.

***1 mmol scale reaction**:* A solution of *p*-TsOH ·H_2O (38 mg, 0.2 mmol, 20 mol %), ynone **1a** (1 mmol, 206 mg) and indole **2a** (4 mmol, 524 mg) in $CHCl_2$ (2 mL) was stirred at 60 °C for 24 h. After cooling to ambient temperature, the mixture was isolated by column chromatography (Petroleum Ether/EtOAc: 100:1) to afford the desired product **3aa** (314 mg, 70%).



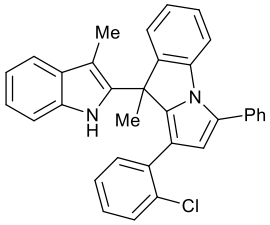
9-methyl-9-(3-methyl-1*H*-indol-2-yl)-3-phenyl-1-(m-tolyl)-9*H*-pyrrolo[1,2-α]indole (3ab)

The general procedure was followed using substrate ynone **1b** and indole **2a** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 120:1) yielded **3ab** (64 mg, 68%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.71 – 7.69 (m, 2H), 7.55 – 7.54 (m, 1H), 7.53 – 7.51 (m, 2H), 7.48 – 7.43 (m, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.20 – 7.16 (m, 2H), 7.14 – 7.09 (m, 3H), 7.06 – 7.00 (m, 3H), 6.91 (d, J = 7.2 Hz, 1H), 6.81 (s, 1H), 6.59 (s, 1H), 2.05 (s, 6H), 2.04 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3, 139.8, 139.1, 138.0, 135.4, 135.1, 134.7, 132.8, 130.4, 129.3, 128.8, 128.6, 128.5, 128.0, 127.9, 127.7, 126.5, 124.5, 124.2, 124.0, 121.7, 119.9, 119.4, 118.5, 114.2, 112.0, 110.7, 108.3, 45.5, 23.2, 21.4, 8.7 ppm. HR-MS (ESI): *m/z* calcd for $C_{34}H_{26}N_2$ $[M+H]^+$ 465.23307, found: 465.23313.



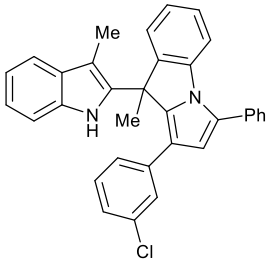
9-methyl-9-(3-methyl-1*H*-indol-2-yl)-3-phenyl-1-(p-tolyl)-9*H*-pyrrolo[1,2-α]indole (3ac)

The general procedure was followed using substrate ynone **1c** and indole **2a** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 120:1) yielded **3ac** (53 mg, 57%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.69 – 7.67 (m, 2H), 7.54 – 7.50 (m, 3H), 7.46 – 7.42 (m, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.22 – 7.20 (m, 1H), 7.19 – 7.15 (m, 1H), 7.13 – 7.08 (m, 3H), 7.05 (d, J = 8.0 Hz, 2H), 7.00 (dd, J = 7.6, 2.0 Hz, 1H), 6.97 – 6.95 (m, 2H), 6.58 (s, 1H), 2.25 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 139.4, 139.0, 135.4, 134.7, 132.8, 132.3, 130.5, 129.4, 129.3, 128.9, 128.6, 127.9, 127.7, 126.9, 124.4, 124.2, 121.7, 119.9, 119.3, 118.5, 114.1, 112.0, 110.7, 108.1, 45.6, 22.9, 21.1, 8.8 ppm. HR-MS (ESI): *m/z* calcd for $C_{34}H_{26}N_2$ $[M+H]^+$ 465.23307, found: 465.23273.



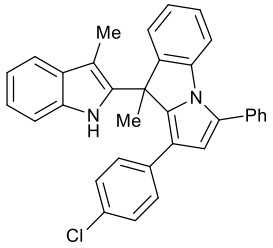
1-(2-chlorophenyl)-9-methyl-9-(3-methyl-1*H*-indol-2-yl)-3-phenyl-9*H*-pyrrolo[1,2-α]indole (3ad)

The general procedure was followed using substrate ynone **1d** and indole **2a** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 100:1) yielded **3ad** (43 mg, 44%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.71 – 7.70 (m, 2H), 7.53 – 7.47 (m, 3H), 7.45 – 7.41 (m, 1H), 7.37 (dd, J = 8.0, 1.2 Hz, 1H), 7.28 – 7.26 (m, 1H), 7.23 – 7.19 (m, 2H), 7.16 – 7.10 (m, 3H), 7.08 – 7.00 (m, 2H), 6.81 (td, J = 7.6, 1.2 Hz, 1H), 6.59 (dd, J = 7.6, 1.6 Hz, 1H), 6.53 (s, 1H), 1.929 (s, 3H), 1.926 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.1, 141.4, 139.6, 135.4, 134.4, 134.0, 133.6, 132.7, 132.0, 130.3, 129.7, 129.2, 128.6, 128.0, 127.9, 127.86, 127.80, 126.3, 124.6, 124.2, 121.6, 119.3, 118.4, 117.0, 116.5, 112.1, 110.6, 108.0, 45.0, 24.2, 8.7 ppm. HR-MS (ESI): *m/z* calcd for $C_{33}H_{25}ClN_2$ $[M+H]^+$ 485.17845, found: 485.17719.



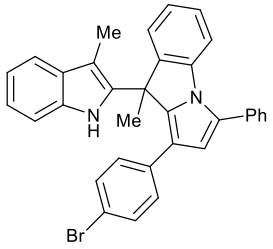
1-(3-chlorophenyl)-9-methyl-9-(3-methyl-1*H*-indol-2-yl)-3-phenyl-9*H*-pyrrolo[1,2-α]indole (3ae)

The general procedure was followed using substrate ynone **1e** and indole **2a** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 100:1) yielded **3ae** (70 mg, 72%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.70 – 7.67 (m, 2H), 7.56 – 7.52 (m, 3H), 7.49 – 7.45 (m, 1H), 7.37 – 7.35 (m, 1H), 7.19 (td, J = 8.4,1.2 Hz, 2H), 7.14 – 7.09 (m, 4H), 7.06 – 6.98 (m, 4H), 6.57 (s, 1H), 2.04 (s, 3H), 2.02 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 140.3, 138.9, 137.1, 134.8, 134.7, 134.4, 132.5, 130.3, 129.8, 129.3, 129.2, 128.7, 128.1, 127.8, 127.1, 125.6, 124.9, 124.48, 124.46, 121.9, 119.5, 118.5, 113.8, 112.1, 110.8, 108.5, 45.5, 23.0, 8.6 ppm. HR-MS (ESI): *m/z* calcd for $C_{33}H_{25}ClN_2$ $[M+H]^+$ 485.17845, found: 485.17771.



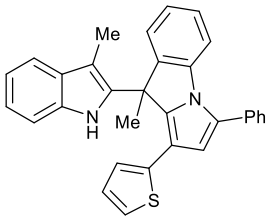
1-(4-chlorophenyl)-9-methyl-9-(3-methyl-1*H*-indol-2-yl)-3-phenyl-9*H*-pyrrolo[1,2-α]indole (3af)

The general procedure was followed using substrate ynone **1f** and indole **2a** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 100:1) yielded **3af** (80 mg, 83%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): 8.05 (s, 1H), 7.68 – 7.64 (m, 2H), 7.52 – 7.44 (m, 4H), 7.33 (dd, *J* = 7.6, 4.4 Hz, 2H), 7.20 – 7.17 (m, 2H), 7.10 – 7.07 (m, 5H), 7.05 – 6.99 (m, 3H), 6.54 (s, 1H), 2.03 – 2.01 (m, 6H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): *δ* 144.2, 139.8, 138.9, 134.9, 134.7, 133.8, 132.6, 131.4, 130.4, 129.3, 129.2, 128.74, 128.70, 128.2, 128.1, 127.8, 124.4, 121.9, 119.5, 118.7, 118.6, 113.9, 112.1, 110.7, 108.4, 45.6, 23.0, 8.7 ppm. HR-MS (ESI): *m/z* calcd for $C_{33}H_{25}ClN_2$ $[M+H]^+$ 485.17845, found: 485.17697.



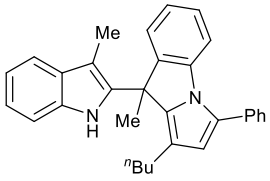
1-(4-bromophenyl)-9-methyl-9-(3-methyl-1*H*-indol-2-yl)-3-phenyl-9*H*-pyrrolo[1,2-α]indole (3ag)

The general procedure was followed using substrate ynone **1g** and indole **2a** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 100:1) yielded **3ag** (82 mg, 78%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.06 (s, 1H), 7.68 – 7.66 (m, 2H), 7.55 – 7.51 (m, 3H), 7.48 – 7.45 (m, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.27 – 7.26 (m, 1H), 7.25 – 7.23 (m, 1H), 7.21 – 7.17 (m, 2H), 7.14 – 7.09 (m, 3H), 7.03 – 7.00 (m, 1H), 6.99 (dd, *J* = 6.8, 2.0 Hz, 2H), 6.55 (s, 1H), 2.04 (s, 3H), 2.02 (s, 3H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): *δ* 144.2, 139.9, 138.8, 134.9, 134.7, 134.3, 132.5, 131.7, 130.3, 129.3, 129.2, 128.7, 128.6, 128.1, 127.8, 124.4, 121.9, 119.52, 119.51, 118.7, 118.6, 113.8, 112.1, 110.7, 108.4, 45.6, 22.9, 8.7 ppm. HR-MS (ESI): *m/z* calcd for $C_{33}H_{25}BrN_2$ $[M+H]^+$ 529.12794, found: 529.12733.



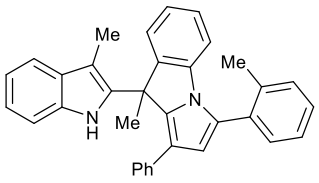
9-methyl-9-(3-methyl-1*H*-indol-2-yl)-3-phenyl-1-(thiophen-2-yl)-9*H*-pyrrolo[1,2-α]indole (3ah)

The general procedure was followed using substrate ynone **1h** and indole **2a** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 100:1) yielded **3ah** (70 mg, 77%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.69 – 7.66 (m, 2H), 7.55 – 7.45 (m, 4H), 7.36 – 7.33 (m, 1H), 7.23 – 7.16 (m, 2H), 7.13 – 7.08 (m, 3H), 7.03 – 6.98 (m, 2H), 6.84 – 6.80 (m, 1H), 6.66 – 6.64 (m, 1H), 6.58 (s, 1H), 2.16 (s, 3H), 2.00 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 139.0, 138.9, 137.7, 134.7, 134.1, 132.4, 130.5, 129.4, 128.9, 128.6, 128.1, 127.7, 127.6, 124.5, 124.4, 123.2, 123.0, 121.7, 119.3, 118.5, 114.0, 113.5, 112.1, 110.8, 108.5, 45.5, 22.8, 8.8 ppm. HR-MS (ESI): *m/z* calcd for $C_{31}H_{24}N_2S$ $[M+H]^+$ 607.03845, found: 607.03830.



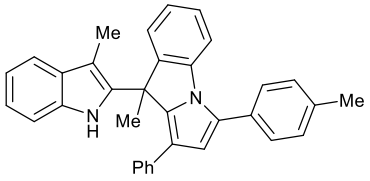
1-butyl-9-methyl-9-(3-methyl-1*H*-indol-2-yl)-3-phenyl-9*H*-pyrrolo[1,2-α]indole (3ai)

The general procedure was followed using substrate ynone **1i** and indole **2a** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 100:1) yielded **3ai** (25 mg, 30%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.64 – 7.61 (m, 2H), 7.50 – 7.46 (m, 3H), 7.41 – 7.38 (m, 1H), 7.28 – 7.22 (m, 2H), 7.16 – 7.12 (m, 2H), 7.10 – 7.06 (m, 2H), 6.97 (td, J = 7.6, 1.2 Hz, 1H), 6.22 (s, 1H), 2.35 – 2.27 (m, 2H), 2.14 (s, 3H), 2.07 (s, 3H), 1.43 – 1.36 (m, 2H), 1.25 – 1.19 (m, 2H), 0.75 (t, J = 7.2 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 140.3, 139.7, 135.1, 134.4, 133.2, 130.5, 128.9, 128.5, 128.1, 127.7, 127.8, 124.5, 123.6, 121.5, 119.2, 118.9, 118.3, 114.9, 111.7, 110.5, 107.8, 44.7, 33.1, 25.3, 25.2, 22.6, 14.0, 9.2 ppm. HR-MS (ESI): *m/z* calcd for $C_{31}H_{30}N_2$ $[M+H]^+$ 431.24872, found: 431,24861.



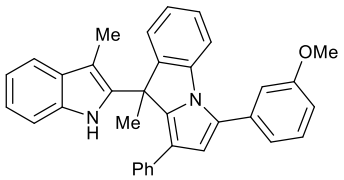
9-methyl-9-(3-methyl-1*H*-indol-2-yl)-1-phenyl-3-(*o*-tolyl)-9*H*-pyrrolo[1,2-α]indole (3aj)

The general procedure was followed using substrate ynone **1j** and indole **2a** to furnish the crude product as a 2:1 mixture of diastereoisomers; d.r. determined by integration of ^{1}H NMR signal: δ_{major} 8.16 (s), δ_{minor} 8.08 (s) ppm. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 120:1) yielded **3aj** (58 mg, 65%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (s, 1H), 7.53 (d, J = 7.2 Hz, 2H), 7.43 – 7.38 (m, 4H), 7.33 (d, J = 8.0 Hz, 1H), 7.19 – 7.15 (m, 7H), 7.10 – 7.08 (m, 1H), 7.02 (dd, J = 7.6, 0.8 Hz, 1H), 6.98 (d, J = 7.2 Hz, 1H), 6.53 (s, 1H), 6.50 (d, J = 7.6 Hz, 1H), 2.37 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 139.0, 138.6, 138.0, 135.5, 135.3, 134.7, 132.6, 131.4, 130.4, 130.2, 129.0, 128.7, 128.0, 127.0, 126.9, 126.8, 126.0, 125.6, 124.2, 124.1, 121.7, 119.44, 119.40, 118.5, 113.3, 110.8, 110.7, 108.28, 108.25, 45.4, 22.7, 20.4, 8.6 ppm. HR-MS (ESI): *m/z* calcd for $C_{34}H_{28}N_2$ $[M+H]^+$ 465.23307, found: 465.23198.



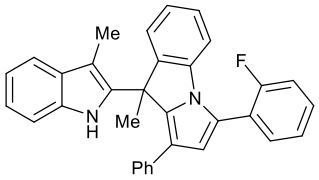
9-methyl-9-(3-methyl-1*H*-indol-2-yl)-1-phenyl-3-(*p*-tolyl)-9*H*-pyrrolo[1,2-α]indole (3ak)

The general procedure was followed using substrate ynone **1k** and indole **2a** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 120:1) yielded **3ak** (42 mg, 45%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.58 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 7.6 Hz, 1H), 7.34 – 7.31 (m, 3H), 7.21 (dd, J = 7.6, 0.4 Hz, 1H), 7.17 – 7.13 (m, 5H), 7.12 – 7.07 (m, 4H), 6.99 (td, J = 7.2, 1.6 Hz, 1H), 6.57 (s, 1H), 2.48 (s, 3H), 2.09 (s, 3H), 2.05 (s, 3H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3, 139.4, 139.0, 137.8, 135.4, 135.3, 134.7, 130.5, 129.8, 129.3, 129.2, 129.1, 128.6, 127.7, 127.0, 125.7, 124.4, 124.2,121.7, 119.8, 119.3, 118.5, 113.8, 112.0, 110.7, 108.1, 45.6, 23.0, 21.5, 8.8 ppm. HR-MS (ESI): *m/z* calcd for $C_{34}H_{28}N_2$ $[M+H]^+$ 465.23307, found: 465.23233.



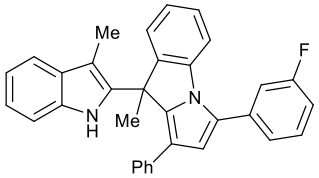
3-(3-methoxyphenyl)-9-methyl-9-(3-methyl-1*H*-indol-2-yl)-1-phenyl-9*H*-pyrrolo[1,2-α]indole (3al)

The general procedure was followed using substrate ynone **1l** and indole **2a** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 100:1) yielded **3al** (66 mg, 69%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.44 (t, J = 8.0 Hz, 1H), 7.34 – 7.27 (m, 3H), 7.23 – 7.21 (m, 2H), 7.19 – 7.18 (m, 1H), 7.16 – 7.15 (m, 4H), 7.14 – 7.09 (m, 3H), 7.03 – 6.99 (m, 2H), 6.62 (s, 1H), 3.91 (s, 3H), 2.08 (s, 3H), 2.05 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 144.3, 139.7, 138.9, 135.3, 135.2, 134.7, 134.0, 130.5, 129.6, 128.9, 128.6, 127.7, 127.0, 125.8, 124.4, 124.3, 121.8, 121.7, 119.9, 119.3, 118.5, 114.6, 114.2, 113.7, 112.1, 110.7, 108.2, 55.5, 45.6, 22.9, 8.8 ppm. HR-MS (ESI): *m/z* calcd for $C_{34}H_{28}N_2O$ $[M+H]^+$ 481.22799, found: 481.22645.



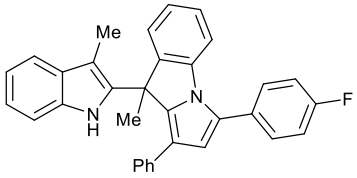
3-(2-fluorophenyl)-9-methyl-9-(3-methyl-1*H*-indol-2-yl)-1-phenyl-9*H*-pyrrolo[1,2-α]indole (3am)

The general procedure was followed using substrate ynone **1m** and indole **2a** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 100:1) yielded **3am** (82 mg, 88%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (s, 1H), 7.64 (td, J = 7.6, 2.0 Hz, 1H), 7.52 (d, J = 7.2 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.36 – 7.27 (m, 3H), 7.22 – 7.18 (m, 2H), 7.17 – 7.15 (m, 4H), 7.14 – 7.09 (m, 3H), 7.01 (t, J = 7.6 Hz, 1H), 6.91 (dd, J = 8.0, 2.4 Hz, 1H), 6.67 (s, 1H), 2.05 (s, 3H), 2.04 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4 (d, J_{CF} = 247.9 Hz), 144.1, 139.8, 138.9, 135.14, 135.10, 134.7, 132.1 (d, J_{CF} = 2.5 Hz), 130.5, 130.1 (d, J_{CF} = 7.9 Hz), 128.6, 127.9, 127.0, 125.8, 124.4 (d, J_{CF} = 3.8 Hz), 124.3 (d, J_{CF} = 4.2 Hz), 121.7, 121.4, 119.9, 119.4, 118.6, 116.2, 116.0, 115.2, 111.5 (d, J_{CF} = 1.9 Hz), 110.7, 108.4, 45.6, 22.7, 8.6 ppm. ^{19}F NMR (376 MHz,$CDCl_3$): δ -113.12 – -113.15 (m) ppm. HR-MS (ESI): *m/z* calcd for $C_{33}H_{25}FN_2$ $[M+H]^+$ 469.20800, found: 469.20791.



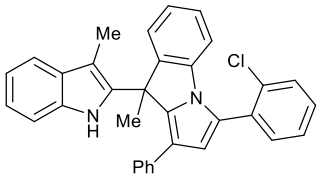
3-(3-fluorophenyl)-9-methyl-9-(3-methyl-1*H*-indol-2-yl)-1-phenyl-9*H*-pyrrolo[1,2-α]indole (3an)

The general procedure was followed using substrate ynone **1n** and indole **2a** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 100:1) yielded **3an** (50 mg, 53%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.53 (d, J = 7.2 Hz, 1H), 7.50 – 7.47 (m, 2H), 7.40 (dd, J = 10.0, 1.6 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.19 – 7.10 (m, 10H), 7.03 (td, J = 7.6, 1.6 Hz, 1H), 6.63 (s, 1H), 2.05 (s, 3H), 2.04 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): 162.8 (d, J_{CF} = 246.6 Hz), 144.2, 140.2, 138.7, 135.0, 134.9, 134.8 (d, J_{CF} = 8.4 Hz), 134.7, 130.4, 130.1 (d, J_{CF} = 8.6 Hz), 128.6, 127.8, 127.0, 125.9, 124.9 (d, J_{CF} = 2.9 Hz), 124.5, 124.4, 121.8, 120.1, 119.4, 118.5, 116.1, 115.9, 114.8, 114.7 (d, J_{CF} = 21.1 Hz), 111.9, 110.7, 108.2, 45.5, 22.9, 8.7 ppm. ^{19}F NMR (376 MHz,$CDCl_3$): δ -112.49 – -112.54 (m) ppm. HR-MS (ESI): *m/z* calcd for $C_{33}H_{25}FN_2$ $[M+H]^+$ 469.20800, found: 469.20660.



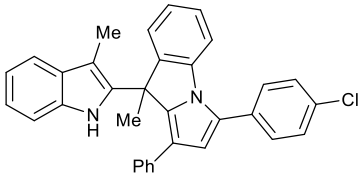
3-(4-fluorophenyl)-9-methyl-9-(3-methyl-1*H*-indol-2-yl)-1-phenyl-9*H*-pyrrolo[1,2-α]indole (3ao)

The general procedure was followed using substrate ynone **1o** and indole **2a** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 100:1) yielded **3ao** (63 mg, 67%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.67 – 7.62 (m, 2H), 7.52 (d, J = 7.6 Hz, 1H), 7.34 – 7.32 (m, 1H), 7.24 – 7.22 (m, 2H), 7.21 – 7.20 (m, 1H), 7.18 – 7.14 (m, 5H), 7.13 – 7.07 (m, 3H), 7.04 – 7.00 (m, 2H), 6.57 (s, 1H), 2.06 (s, 3H), 2.05 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7 (d, J_{CF} = 247.5 Hz), 142.3, 137.6, 136.8, 133.1 (d, J_{CF} = 7.4 Hz), 132.7, 129.1 (d, J_{CF} = 8.1 Hz), 128.5, 126.7, 125.8, 125.8, 125.0, 123.8, 122.4 (d, J_{CF} = 19.4 Hz), 119.8, 117.9, 117.4, 116.5, 113.7 (d, J_{CF} = 21.6 Hz), 112.1, 109.7, 108.7, 106.2, 43.6, 20.9, 6.8 ppm. ^{19}F NMR (376 MHz,$CDCl_3$): δ -115.67 – -115.73 (m) ppm. HR-MS (ESI): *m/z* calcd for $C_{33}H_{25}FN_2$ $[M+H]^+$ 469.20800, found: 469.20795.



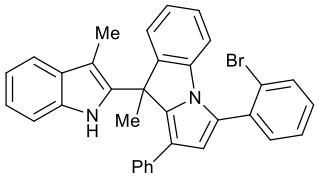
3-(2-chlorophenyl)-9-methyl-9-(3-methyl-1*H*-indol-2-yl)-1-phenyl-9*H*-pyrrolo[1,2-α]indole (3ap)

The general procedure was followed using substrate ynone **1p** and indole **2a** to furnish the crude product as a 2.5:1 mixture of diastereoisomers; d.r. determined by integration of ^{1}H NMR signal: δ_{major} 8.10 (s), δ_{minor} 8.09 (s) ppm. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 100:1) yielded **3ap** (75 mg, 78%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 1H), 7.65 (dd, J = 6.8, 2.0 Hz,2H), 7.60 – 7.59 (m, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.46 – 7.43 (m, 2H), 7.37 – 7.32 (m, 1H), 7.17 – 7.14 (m, 6H), 7.10 – 7.09 (m, 1H), 7.07 – 7.05 (m, 1H), 7.01 – 6.97 (m, 1H), 6.63 (d, J = 7.6 Hz, 1H), 6.60 (s, 1H), 2.07 (s, 3H), 2.04 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 139.0, 138.8, 135.3, 135.0, 134.7, 132.8, 132.1, 130.5, 130.1, 129.9, 128.7, 127.9, 127.0, 125.7, 124.6, 124.2, 124.1, 121.7, 119.4, 118.6, 114.4, 111.3, 110.7, 108.5, 45.6, 22.6, 8.8 ppm. HR-MS (ESI): *m/z* calcd for $C_{33}H_{25}ClN_2$ $[M+H]^+$ 485.17845, found: 485.17733.



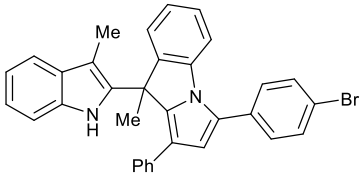
3-(4-chlorophenyl)-9-methyl-9-(3-methyl-1*H*-indol-2-yl)-1-phenyl-9*H*-pyrrolo[1,2-α]indole (3aq)

The general procedure was followed using substrate ynone **1q** and indole **2a** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 100:1) yielded **3aq** (77 mg, 80%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.62 (d, J = 8.4 Hz, 2H), 7.53 – 7.49 (m, 3H), 7.34 – 7.32 (m, 2H), 7.22 (d, J = 7.6 Hz, 1H), 7.17 – 7.09 (m, 8H), 7.04 – 7.00 (m, 1H), 6.59 (s, 1H), 2.05 (s, 3H), 2.04 (s, 3H) ppm. ^{13}C NMR (100 MHz,$CDCl_3$): δ 144.3, 140.0, 138.8, 135.1, 135.0, 134.7, 133.9, 131.2, 130.5, 130.4, 128.9, 128.7, 127.8, 127.7, 127.0, 125.9, 124.6, 124.4, 121.8, 120.1, 119.4, 118.5, 114.5, 111.8, 110.7, 108.2, 45.6, 22.9, 8.8 ppm. HR-MS (ESI): *m/z* calcd for $C_{33}H_{25}ClN_2$ $[M+H]^+$ 485.17845, found: 485.17712.



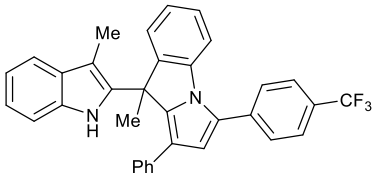
3-(2-bromophenyl)-9-methyl-9-(3-methyl-1*H*-indol-2-yl)-1-phenyl-9*H*-pyrrolo[1,2-α]indole (3ar)

The general procedure was followed using substrate ynone **1r** and indole **2a** to furnish the crude product as a 2:1 mixture of diastereoisomers; d.r. determined by integration of ^{1}H NMR signal: δ_{major} 6.60 (s), δ_{minor} 6.67 (s) ppm. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 100:1) yielded **3ar** (65 mg, 62%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.78 (d, J = 1.2 Hz, 1H), 7.64 (dd, J = 5.6, 2.0 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.39 – 7.35 (m, 2H), 7.20 – 7.16 (m, 7H), 7.10 – 7.09 (m, 1H), 7.07 (d, J = 1.2 Hz, 1H), 7.00 (dd, J = 7.6, 0.8 Hz, 1H), 6.60 (s, 1H), 6.58 (d, J = 7.6 Hz, 1H), 2.13 (s, 3H), 2.05 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 138.7, 138.7, 135.2, 135.1, 134.7, 134.2, 133.0, 133.0, 130.4, 130.3, 128.7, 128.6, 127.9, 127.6, 126.9, 126.2, 125.9, 125.7, 124.2, 124.1, 121.7, 119.4, 119.3, 118.6, 114.2, 111.3, 110.7, 108.4, 45.7, 22.6, 9.2 ppm. HR-MS (ESI): *m/z* calcd for $C_{33}H_{25}BrN_2$ $[M+H]^+$ 529.12794, found: 529.12773.



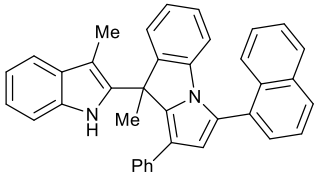
3-(4-bromophenyl)-9-methyl-9-(3-methyl-1*H*-indol-2-yl)-1-phenyl-9*H*-pyrrolo[1,2-α]indole (3as)

The general procedure was followed using substrate ynone **1s** and indole **2a** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 100:1) yielded **3as** (79 mg, 75%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.67 – 7.65 (m, 2H), 7.57 – 7.51 (m, 3H), 7.35 – 7.32 (m, 1H), 7.22 (dd, J = 7.6, 1.2 Hz, 1H), 7.19 – 7.09 (m, 9H), 7.05 – 7.00 (m, 1H), 6.60 (s, 1H), 2.05 (s, 3H), 2.04 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3, 140.1, 138.7, 135.0, 135.0, 134.7, 131.8, 131.7, 130.7, 130.4, 128.7, 127.8, 127.7, 127.0, 125.9, 124.6, 124.5, 122.0, 121.8, 120.2, 119.4, 118.5, 114.5, 111.8, 110.7, 108.2, 45.6, 22.9, 8.8 ppm. HR-MS (ESI): *m/z* calcd for $C_{33}H_{25}BrN_2$ $[M+H]^+$ 529.12794, found: 529.12657.



9-methyl-9-(3-methyl-1*H*-indol-2-yl)-1-phenyl-3-(4-(trifluoromethyl)phenyl)-9*H*-pyrrolo[1,2-*α*]indole (3at)

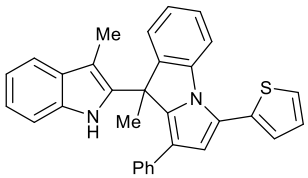
The general procedure was followed using substrate ynone **1t** and indole **2a** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 100:1) yielded **3at** (80 mg, 77%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.80 (dd, J = 12.4, 8.4 Hz 4H), 7.52 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.21 – 7.11 (m, 9H), 7.06 – 7.02 (m, 1H), 6.66 (s, 1H), 2.04 (s, 3H), 2.04 (s, 3H) ppm,^{13}C NMR (100 MHz, $CDCl_3$): δ144.3, 140.9, 138.7, 136.3, 134.87, 134.85, 134.7, 130.4, 129.8, 129.5, 129.1, 128.7, 127.9, 127.5, 127.1, 126.0, 125.7 (q, J_{CF} = 3.8 Hz), 124.6, 124.4 (q, J_{CF} = 271.9 Hz), 121.9, 120.5, 119.5, 118.6, 115.5, 111.9, 110.7, 108.3, 45.6, 23.0, 8.7 ppm.^{19}F NMR (376 MHz, $CDCl_3$): δ -62.24 (s) ppm. HR-MS (ESI): *m/z* calcd for $C_{34}H_{25}F_3N_2$ $[M+H]^+$ 519.20481, found: 519.20470.



9-methyl-9-(3-methyl-1*H*-indol-2-yl)-3-(naphthalen-1-yl)-1-phenyl-9*H*-pyrrolo[1,2-*α*]indole (3au)

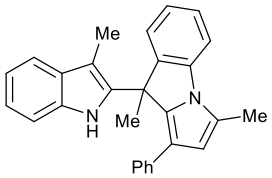
The general procedure was followed using substrate ynone **1u** and indole **2a** to furnish the crude product as a 1.5:1 mixture of diastereoisomers; d.r. determined by integration of ^{1}H NMR signal: δ_{major} 8.20 (s), δ_{minor} 8.11 (s) ppm. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 100:1) yielded **3au** (79 mg, 79%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.20 (s, 1H), 8.01 (dd, J = 12.0, 8.4 Hz, 4H), 7.76 (dd, J = 4.0, 1.2 Hz, 1H), 7.65 (d, J = 7.2 Hz, 1H), 7.56 – 7.53 (m, 3H), 7.51 – 7.48 (m, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.19 – 7.15 (m, 6H), 6.91 – 6.88 (m, 1H), 6.87 – 6.85 (m, 1H), 6.72 (s, 1H), 6.16 (d, J = 7.6 Hz, 1H), 2.10 (s, 3H), 2.08 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.0, 138.9, 138.7, 135.4, 135.2, 134.7, 133.8, 133.2, 130.5, 130.4, 129.12, 129.10, 128.7, 128.5, 127.7, 127.0, 126.9, 126.4, 126.3, 125.8, 125.7, 125.5, 124.1, 124.0, 121.7, 119.7, 119.5, 118.6, 115.1, 111.8,

110.8, 108.3, 45.6, 22.9, 8.8 ppm. HR-MS (ESI): *m/z* calcd for $C_{37}H_{28}N_2$ $[M+H]^+$ 501.23307, found: 501.23289.



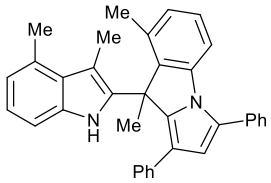
9-methyl-9-(3-methyl-1*H*-indol-2-yl)-1-phenyl-3-(thiophen-2-yl)-9*H*-pyrrolo[1,2-α]indole (3av)

The general procedure was followed using substrate ynone **1v** and indole **2a** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 100:1) yielded **3av** (61 mg, 67%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.47 (dd, J = 5.2, 1.2 Hz, 1H), 7.35 (dd, J = 3.6, 1.2 Hz, 1H), 7.33 (d, J = 8.0 Hz, 1H), 7.23 – 7.18 (m, 4H), 7.17 – 7.11 (m, 7H), 7.03 (td, J = 7.6, 1.2 Hz, 1H), 6.70 (s, 1H), 2.08 (s, 3H), 2.05 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 139.8, 138.7, 135.0, 134.9, 134.7, 133.6, 130.4, 128.7, 128.2, 127.9, 127.5, 127.0, 126.4, 125.9, 124.44, 124.43, 121.8, 120.3, 119.9, 119.4, 118.5, 116.0, 111.8, 110.7, 108.3, 45.9, 22.9, 8.9 ppm. HR-MS (ESI): *m/z* calcd for $C_{31}H_{24}N_2S$ $[M+H]^+$ 457.17384, found: 457.17245.



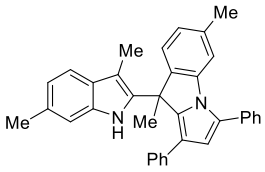
3,9-dimethyl-9-(3-methyl-1*H*-indol-2-yl)-1-phenyl-9*H*-pyrrolo[1,2-α]indole (3aw)

The general procedure was followed using substrate ynone **1w** and indole **2a** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 100:1) yielded **3aw** (25 mg, 32%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.40 (d, J = 8.0 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.22 – 7.20 (m, 1H), 7.13 (dd, J = 7.2, 1.2 Hz, 1H), 7.11 – 7.10 (m, 4H), 7.08 – 6.99 (m, 3H), 6.32 (s, 1H), 2.67 (s, 3H), 2.07 (s, 3H), 2.00 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3, 139.2, 137.6, 135.6, 135.4, 134.7, 130.5, 128.6, 128.0, 126.7, 125.4, 124.7, 123.8, 123.6, 121.6, 119.2, 118.6, 118.5, 111.8, 110.74, 110.70, 108.0, 46.0, 23.1, 13.5, 9.0 ppm. HR-MS (ESI): *m/z* calcd for $C_{28}H_{24}N_2$ $[M+H]^+$ 389.20177, found: 389.20156.



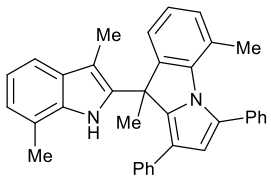
9-(3,4-dimethyl-1*H*-indol-2-yl)-8,9-dimethyl-1,3-diphenyl-9*H*-pyrrolo[1,2-*α*]indole (3ba)

The general procedure was followed using substrate ynone **1a** and indole **2b** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 120:1) yielded **3ba** (58 mg, 61%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.67 – 7.64 (m, 2H), 7.53 – 7.49 (m, 2H), 7.46 – 7.41 (m, 1H), 7.27 – 7.25 (m, 1H), 7.11 – 7.06 (m, 4H), 7.05 – 7.00 (m, 2H), 6.92 – 6.90 (m, 2H), 6.83 – 6.80 (m, 2H), 6.51 (s, 1H), 2.65 (s, 3H), 1.99 (s, 3H), 1.95 (s, 6H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.6, 140.1, 139.7, 135.6, 135.5, 134.9, 133.6, 133.0, 131.1, 129.4, 128.5, 128.4, 128.2, 127.8, 127.5, 126.5, 125.6, 121.5, 121.4, 118.9, 114.7, 110.1, 109.9, 108.9, 44.9, 21.4, 20.8, 17.9, 10.7 ppm. HR-MS (ESI): *m/z* calcd for $C_{35}H_{30}N_2$ $[M+H]^+$ 479.24872, found: 479.24837.



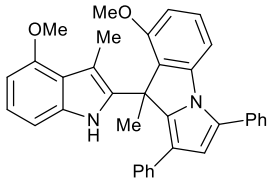
9-(3,6-dimethyl-1*H*-indol-2-yl)-6,9-dimethyl-1,3-diphenyl-9*H*-pyrrolo[1,2-*α*]indole (3ca)

The general procedure was followed using substrate ynone **1a** and indole **2c** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 120:1) yielded **3ca** (90 mg, 94%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.72 – 7.69 (m, 2H), 7.56 – 7.52 (m, 2H), 7.49 – 7.44 (m, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.22 – 7.15 (m, 4H), 7.12 – 7.08 (m, 3H), 6.97 – 6.95 (m, 2H), 6.84 – 6.81 (m, 1H), 6.61 (s, 1H), 2.48 (s, 3H), 2.25 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.7, 140.3, 139.0, 137.6, 135.3, 135.2, 134.7, 132.8, 131.4, 129.3, 128.9, 128.6, 128.5, 128.4, 127.9, 127.0, 125.7, 124.9, 124.0, 121.0, 119.8, 118.2, 114.1, 112.7, 110.7, 107.8, 45.4, 22.9, 21.9, 21.8, 8.9 ppm. HR-MS (ESI): *m/z* calcd for $C_{35}H_{30}N_2$ $[M+H]^+$ 479.24872, found: 479.24832.



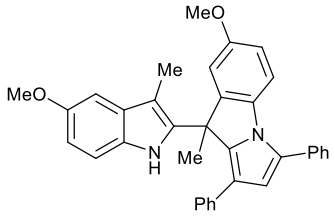
9-(3,7-dimethyl-1*H*-indol-2-yl)-5,9-dimethyl-1,3-diphenyl-9*H*-pyrrolo[1,2-α]indole (3da)

The general procedure was followed using substrate ynone **1a** and indole **2d** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 120:1) yielded **3da** (40 mg, 42%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (s, 1H), 7.62 (d, J = 7.2 Hz, 1H), 7.52 (d, J = 7.2 Hz, 1H), 7.47 – 7.37 (m, 4H), 7.17 – 7.07 (m, 7H), 7.02 – 6.96 (m, 3H), 6.57 (s, 1H), 2.53 (s, 3H), 2.04 (s, 3H), 1.95 (s, 3H), 1.77 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.9, 140.7, 138.6, 135.8, 135.6, 135.4, 134.1, 131.8, 130.0, 129.9, 129.3, 129.2, 128.5, 128.4, 128.3, 127.7, 127.4, 125.7, 124.4, 122.4, 122.3, 121.9, 119.8, 119.6, 119.2, 116.3, 116.2, 108.8, 44.8, 23.7, 21.5, 16.8, 8.7 ppm. HR-MS (ESI): *m/z* calcd for $C_{35}H_{30}N_2$ $[M+H]^+$ 479.24872, found: 479.24861.



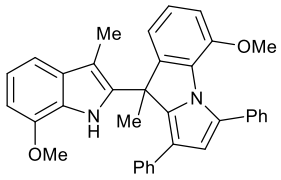
8-methoxy-9-(4-methoxy-3-methyl-1*H*-indol-2-yl)-9-methyl-1,3-diphenyl-9*H*-pyrrolo[1,2-α]indole (3ea)

The general procedure was followed using substrate ynone **1a** and indole **2e** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 60:1) yielded **3ea** (92 mg, 92%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (s, 1H), 7.68 – 7.65 (m, 2H), 7.52 – 7.48 (m, 2H), 7.45 – 7.41 (m, 1H), 7.16 – 7.15 (m, 4H), 7.11 – 7.00 (m, 4H), 6.74 (dd, J = 8.0, 0.4 Hz, 1H), 6.57 (s, 1H), 6.54 (d, J = 8.4 Hz, 1H), 6.47 (d, J = 7.2 Hz, 1H), 3.85 (s, 3H), 3.68 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2, 155.2, 140.5, 140.1, 136.4, 135.5, 133.1, 132.9, 129.4, 129.24, 129.20, 128.65, 128.60, 128.5, 127.7, 127.2, 125.5, 121.7, 119.6, 119.4, 114.2, 108.8, 107.5, 105.4, 104.3, 99.6, 55.8, 55.2, 44.6, 19.8, 9.9 ppm. HR-MS (ESI): *m/z* calcd for $C_{35}H_{30}N_2O_2$ $[M+H]^+$ 511.23855, found: 511.23791.



7-methoxy-9-(5-methoxy-3-methyl-1*H*-indol-2-yl)-9-methyl-1,3-diphenyl-9*H*-pyrrolo[1,2-α]indole (3fa)

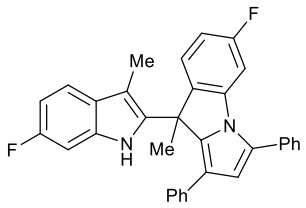
The general procedure was followed using substrate ynone **1a** and indole **2f** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 60:1) yielded **3fa** (78 mg, 78%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (s, 1H), 7.68 – 7.66 (m, 2H), 7.53 – 7.49 (m, 2H), 7.46 – 7.41 (m, 1H), 7.23 (d, J = 8.8 Hz, 1H), 7.17 – 7.08 (m, 5H), 7.05 (d, J = 8.8 Hz, 1H), 6.96 (d, J = 2.4 Hz, 1H), 6.84 (dd, J = 8.8, 2.8 Hz, 1H), 6.78 (d, J = 2.4 Hz, 1H), 6.62 (dd, J = 8.8, 2.4 Hz, 1H), 6.57 (s, 1H), 3.87 (s, 3H), 3.71 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0, 154.1, 145.8, 139.6, 136.2, 135.4, 132.84, 132.80, 130.9, 129.8, 129.2, 128.6, 128.59, 128.58, 127.8, 127.0, 125.6, 119.8, 113.4, 112.4, 112.3, 111.8, 111.5, 110.9, 108.1, 100.5, 56.0, 55.8, 45.8, 23.0, 8.8 ppm. HR-MS (ESI): *m/z* calcd for $C_{35}H_{30}N_2O_2$ $[M+H]^+$ 511.23855, found: 511.23832.



5-methoxy-9-(7-methoxy-3-methyl-1*H*-indol-2-yl)-9-methyl-1,3-diphenyl-9*H*-pyrrolo[1,2-α]indole (3ga)

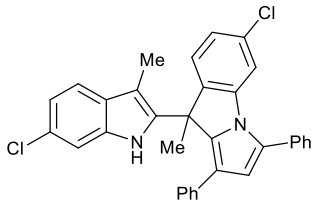
The general procedure was followed using substrate ynone **1a** and indole **2g** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 60:1) yielded **3ga** (51 mg, 51%) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (s, 1H), 7.51 (d, J = 6.8 Hz, 2H), 7.43 – 7.39 (m, 2H), 7.38 – 7.34 (m, 1H), 7.13 – 7.05 (m, 6H), 7.04 – 7.00 (m, 1H), 6.96 (t, J = 8.0 Hz, 1H), 6.80 (d, J = 7.6 Hz, 1H), 6.69 (d, J = 8.4 Hz, 1H), 6.64 (d, J = 7.6 Hz, 1H), 6.53 (s, 1H), 3.99 (s, 3H), 3.22 (s, 3H), 2.01 (s, 3H), 1.94 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.91, 145.90, 145.8, 139.3, 136.1, 135.5, 135.3, 131.8, 130.1, 128.6, 128.1, 127.1, 126.9, 126.8, 125.5, 125.3, 125.0, 119.6, 119.2, 116.4, 114.9, 111.5, 111.3, 108.8, 101.7, 55.4, 55.0, 45.4, 23.0, 8.7 ppm. HR-MS (ESI): *m/z* calcd for

$C_{35}H_{30}N_2O_2$ $[M+H]^+$ 511.23855, found: 511.23820.



6-fluoro-9-(6-fluoro-3-methyl-1*H*-indol-2-yl)-9-methyl-1,3-diphenyl-9*H*-pyrrolo[1,2-α]indole (3ha)

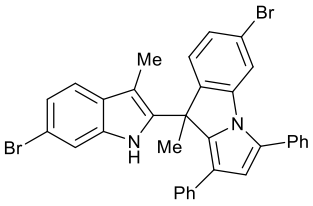
The general procedure was followed using substrate ynone **1a** and indole **2h** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 120:1) yielded **3ha** (78 mg, 80%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (s, 1H), 7.66 – 7.63 (m, 2H), 7.56 – 7.51 (m, 2H), 7.49 – 7.46 (m, 1H), 7.40 (dd, J = 8.4, 5.2 Hz, 1H), 7.18 – 7.10 (m, 6H), 7.01 (dd, J = 9.6, 2.4 Hz, 1H), 6.90 – 6.85 (m, 1H), 6.82 (dd, J = 9.6, 2.4 Hz, 1H), 6.70 (td, J = 8.8, 2.4 Hz, 1H), 6.59 (s, 1H), 2.03 (s, 3H), 2.01 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.4 (d, J_{CF} = 240.4 Hz), 160.0 (d, J_{CF} = 233.2 Hz), 140.2, 139.9 (d, J_{CF} = 12.0 Hz), 139.7 (d, J_{CF} = 3.0 Hz), 134.9, 134.5 (d, J_{CF} = 12.5 Hz), 132.2, 129.22, 129.20, 128.8, 128.7, 127.1, 126.9, 126.0, 125.1 (d, J_{CF} = 10.1 Hz), 120.3, 119.3 (d, J_{CF} = 10.2 Hz), 114.6, 110.6 (d, J_{CF} = 23.0 Hz), 108.1 (d, J_{CF} = 20.9 Hz), 100.7, 100.4, 97.3, 97.0, 45.2, 23.1, 8.8 ppm. ^{19}F NMR (376 MHz,$CDCl_3$): δ -112.73 – -112.80 (m), -121.35 – -121.42 (m) ppm. HR-MS (ESI): *m/z* calcd for $C_{33}H_{24}F_2N_2$ $[M+H]^+$ 487.19858, found: 487.19754.



6-chloro-9-(6-chloro-3-methyl-1*H*-indol-2-yl)-9-methyl-1,3-diphenyl-9*H*-pyrrolo[1,2-α]indole (3ia)

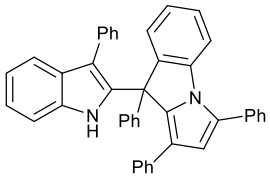
The general procedure was followed using substrate ynone **1a** and indole **2i** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 120:1) yielded **3ia** (67 mg, 65%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H), 7.66 – 7.63 (m, 2H), 7.56 – 7.52 (m, 2H), 7.49 – 7.45 (m, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.31 (dd, J = 1.6, 0.4 Hz, 1H), 7.17 – 7.13 (m, 2H), 7.12 – 7.06 (m, 6H), 6.98 (dd, J = 8.4, 2.0 Hz, 1H), 6.59 (s, 1H), 2.00 (s, 3H), 1.99 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.5, 139.9, 139.5, 135.4, 135.0, 134.8, 133.5, 132.1, 129.3, 129.2,

129.0, 128.8, 128.7, 128.4, 127.8, 127.0, 126.1, 125.1, 124.2, 120.4, 120.3, 119.5, 114.8, 112.6, 110.7, 108.6, 45.2, 23.0, 8.7 ppm. HR-MS (ESI): *m/z* calcd for $C_{33}H_{24}Cl_2N_2$ $[M+H]^+$ 519.13948, found: 519.13868.



6-bromo-9-(6-bromo-3-methyl-1*H*-indol-2-yl)-9-methyl-1,3-diphenyl-9*H*-pyrrolo[1,2-α]indole (3ja)

The general procedure was followed using substrate ynone **1a** and indole **2j** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 120:1) yielded **3ja** (102 mg, 84%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1H), 7.66 – 7.63 (m, 2H), 7.56 – 7.53 (m, 2H), 7.50 – 7.47 (m, 2H), 7.36 (d, J = 8.4 Hz, 1H), 7.25 (d, J = 1.6 Hz, 1H), 7.21 (dd, J = 8.4, 1.6 Hz, 1H), 7.17 – 7.08 (m, 6H), 7.03 (d, J = 8.0 Hz, 1H), 6.60 (s, 1H), 2.00 (s, 3H), 1.99 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.0, 140.1, 139.3, 135.4, 135.3, 134.7, 132.1, 129.3, 129.23, 129.20, 128.8, 128.7, 128.4, 127.1, 127.0, 126.1, 125.5, 122.9, 121.3, 120.4, 119.9, 115.39, 115.36, 114.8, 113.7, 108.6, 45.2, 22.86, 8.7 ppm. HR-MS (ESI): *m/z* calcd for $C_{33}H_{24}Br_2N_2$ $[M+H]^+$ 607.03845, found: 607.03830.

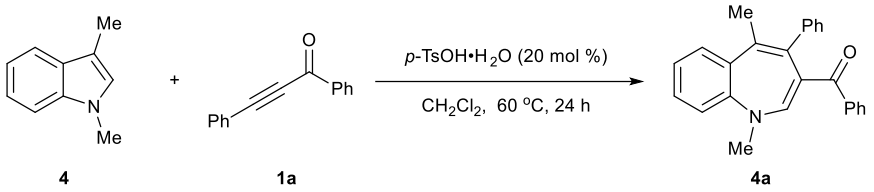


1,3,9-triphenyl-9-(3-phenyl-1*H*-indol-2-yl)-9*H*-pyrrolo[1,2-α]indole (3ka)

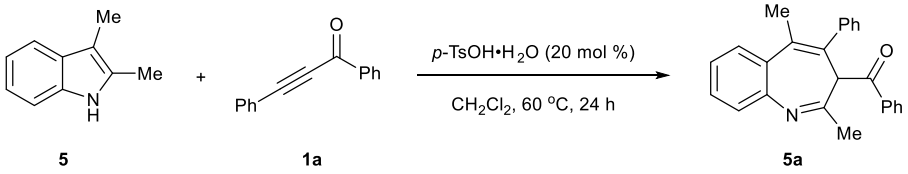
The general procedure was followed using substrate ynone **1a** and indole **2k** to furnish the crude product. The title compound was isolated by column chromatography (Petroleum Ether/EtOAc: 100:1) yielded **3ka** (48 mg, 44%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (s, 1H), 7.61 – 7.58 (m, 2H), 7.57 – 7.54 (m, 2H), 7.52 – 7.48 (m, 1H), 7.46 – 7.42 (m, 1H), 7.33 – 7.29 (m, 4H), 7.20 – 7.19 (m, 2H), 7.15 – 7.10 (m, 4H), 7.09 – 7.03 (m, 3H), 7.00 – 6.98 (m, 3H), 6.86 (dd, J = 7.6, 1.2 Hz, 1H), 6.80 (d, J = 7.6 Hz, 1H), 6.74 – 6.70 (m, 3H), 6.45 (s, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.3, 141.7, 139.5, 138.3, 135.9, 135.0, 134.7, 134.0, 132.7, 130.3, 129.7, 129.3, 128.91, 128.90, 128.5, 128.49, 128.45, 128.3,

127.79, 127.75, 127.6, 127.4, 126.8, 126.2, 125.7, 123.5, 122.2, 121.6, 120.0, 119.5, 116.5, 115.3, 111.7, 110.7, 54.8 ppm. HR-MS (ESI): *m/z* calcd for $C_{43}H_{30}N_2$ $[M+H]^+$ 575.24872, found: 575.24774.

3. Control Experiments



A solution of *p*-TsOH H_2O (7.6 mg, 0.04 mmol, 20 mol%), ynone **1a** (0.2 mmol) and indole **4** (0.8 mmol) in CH_2Cl_2 (0.4 mL) was stirred at 60 °C for 24 h. After cooling to ambient temperature, the mixture was purified by column chromatography (Petroleum Ether /EtOAc: 60:1) yielded **4a** (28 mg, 40%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.43 (m, 2H), 7.34 – 7.32 (m, 2H), 7.24 – 7.20 (m, 3H), 7.15 – 7.10 (m, 3H), 7.08 – 7.05 (m, 1H), 7.04 – 7.01 (m, 2H), 6.94 (s, 1H), 6.90 (d, J = 8.0 Hz, 1H), 3.16 (s, 3H), 2.11 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.0, 156.1, 153.9, 141.2, 139.6, 139.0, 137.2, 136.9, 131.4, 129.9, 129.0, 128.4, 127.9, 127.7, 126.7, 124.2, 116.4, 39.9, 22.4 ppm. HR-MS (ESI): *m/z* calcd for $C_{25}H_{21}NO$ $[M+H]^+$ 352.17014, found: 352.16891. The analytical data are in accordance with these reported in the literature.[3]



A solution of *p*-TsOH H_2O (7.6 mg, 0.04 mmol, 20 mol %), ynone **1a** (0.2 mmol) and indole **5** (0.8 mmol) in CH_2Cl_2 (0.4 mL) was stirred at 60 °C for 24 h. After cooling to ambient temperature, the mixture was purified by column chromatography (Petroleum Ether /EtOAc: 60:1) yielded **5a** (18 mg, 26%) as a yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 – 7.82 (m, 2H), 7.66 (dd, J = 8.4, 1.6 Hz, 1H), 7.51 (dd, J = 8.4, 1.6 Hz, 1H), 7.43 – 7.38 (m, 3H), 7.37 – 7.32 (m, 4H), 7.23 – 7.18 (m, 3H), 4.94 (s, 1H), 2.16 (s, 3H), 1.84 (s, 3H) ppm.^{13}C NMR (100 MHz, $CDCl_3$): δ 202.8, 160.4, 146.7, 142.9, 138.6, 135.0, 132.6, 132.5, 130.6, 128.9, 128.8, 128.6, 128.2, 127.7, 127.44, 127.40, 127.3, 124.8, 62.5, 28.2, 19.8 ppm. HR-MS (ESI): *m/z* calcd for $C_{25}H_{21}NO$ $[M+H]^+$ 352.17014, found: 352.16941.

4. Intermediate Characterization

HR-MS studies of the *p*-TsOH·H_2O catalyzed cascade reaction

The HR-MS analysis refers to the reaction under the optimal conditions.

Ynone **1a** (0.2 mol), 3-methyl-1*H*-indole **2a** (0.8 mol) and 20 mol % of *p*-TsOH·H_2O in CH_2Cl_2 (0.4 mL) at 60 ºC. The crude mixture of the reaction was collected 10 minutes after the start of the reaction. As detailed in Figure S1, the HR-MS spectrum in positive mode of the reaction mixture showed the presence of the intermediate **II** at 338.1535 $[M + H]^+$ and 360.1351 $[M + Na]^+$. The results indicated that the intermediate **II** was formed by the Friedel-Crafts alkenylation of substrates **1a** with **2a**.

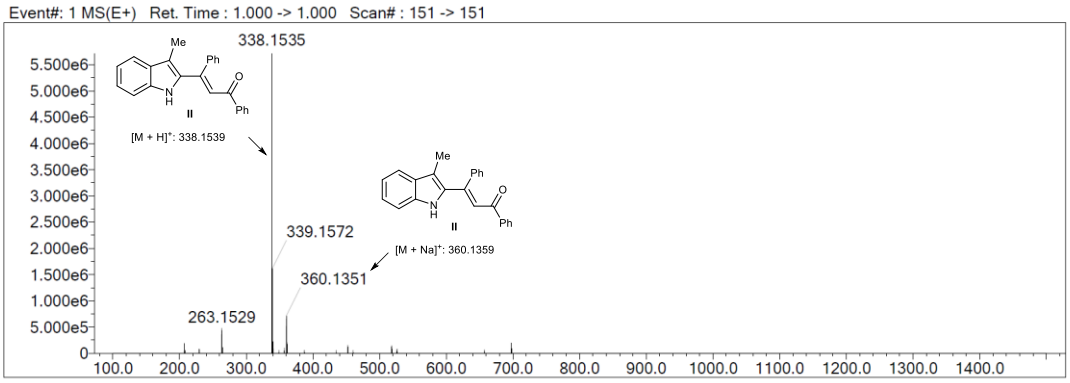


Figure S1. Detectable intermediates by HR-MS analysis in positive mode of the catalytic reaction of **1a** and **2a**. The analyzed sample was collected 10 minutes after the start of the reaction.

A second HR-MS spectrum in positive mode, detailed in Figure S2, was measured 30 minutes after the start of the catalytic reaction.

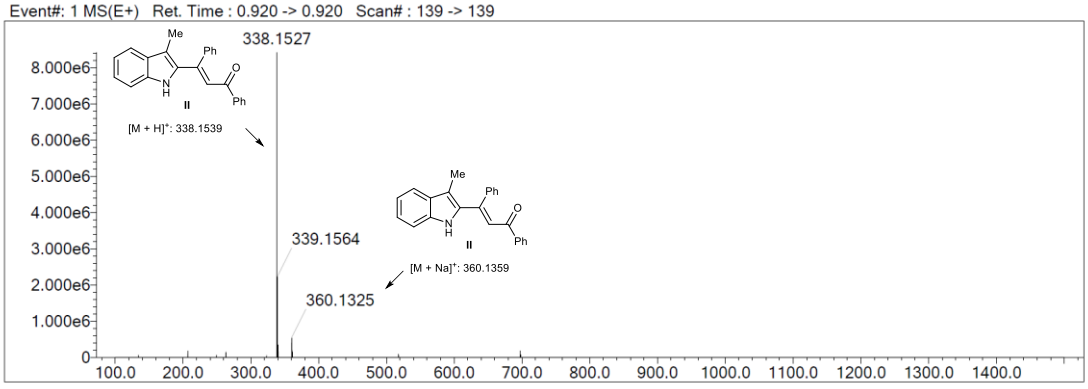


Figure S2. Detectable intermediates by HR-MS analysis in positive mode of the catalytic reaction of **1a** and **2a**. The analyzed sample was collected 30 minutes after the start of the reaction.

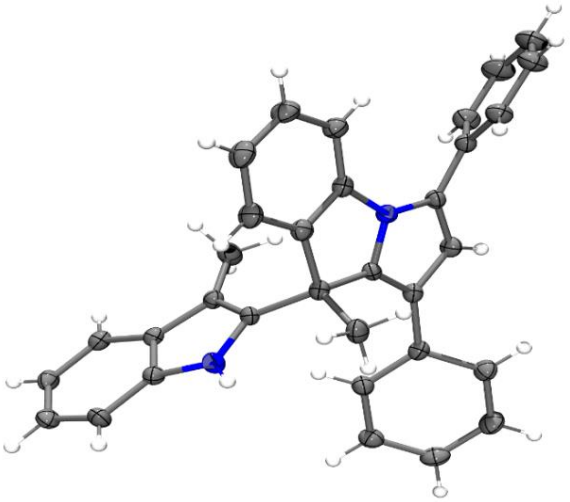
5. References

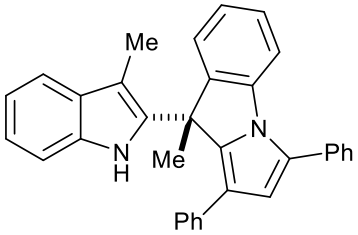
1. K. Okamoto, T. Shimbayashi, E. Tamura and K. Ohe, *Org. Lett.*, 2015, **17**, 5843.

2. Z. Liu, Z. Yang, X. Yu, H. Zhang, B. Yu, Y. Zhao and Z. Liu, *Org. Lett.*, 2017, **19**, 5228.

3. T. R. Pradhan, H. W. Kim and J. K. Park, *Org. Lett.*, 2018, **20**, 5286.

6. Crystal data of 3aa



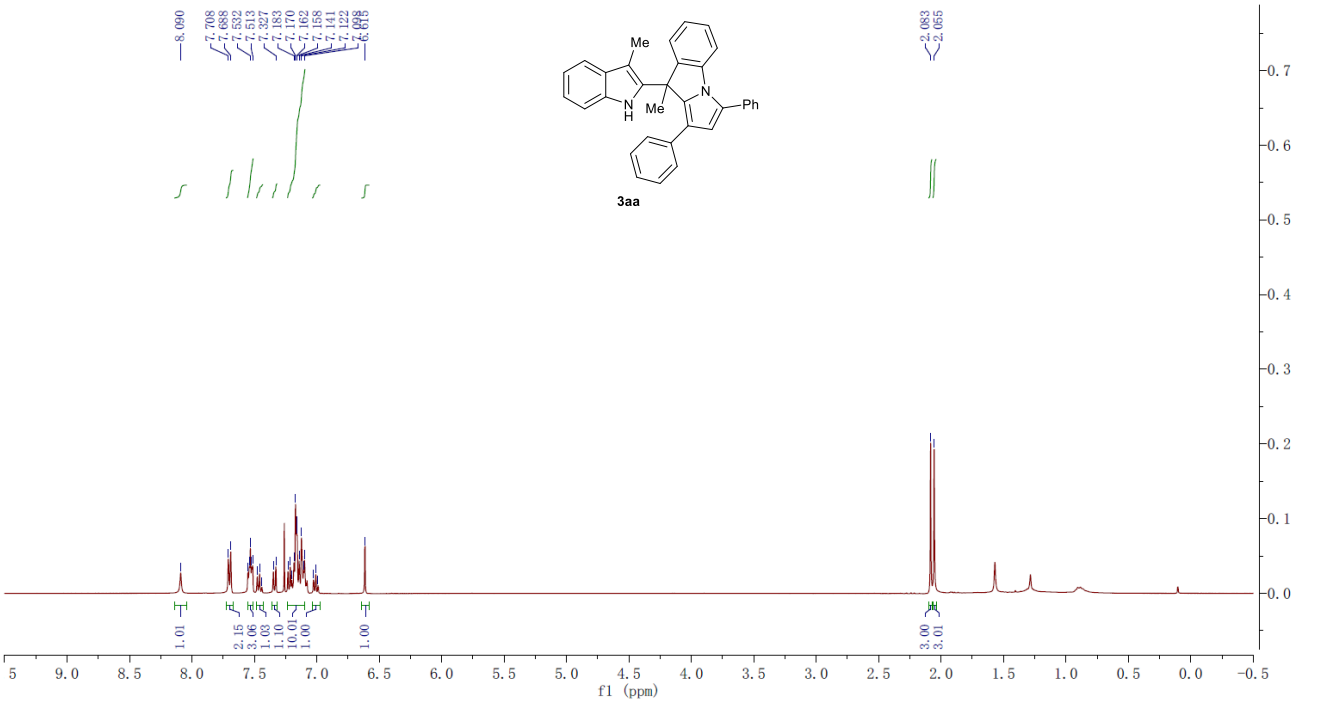


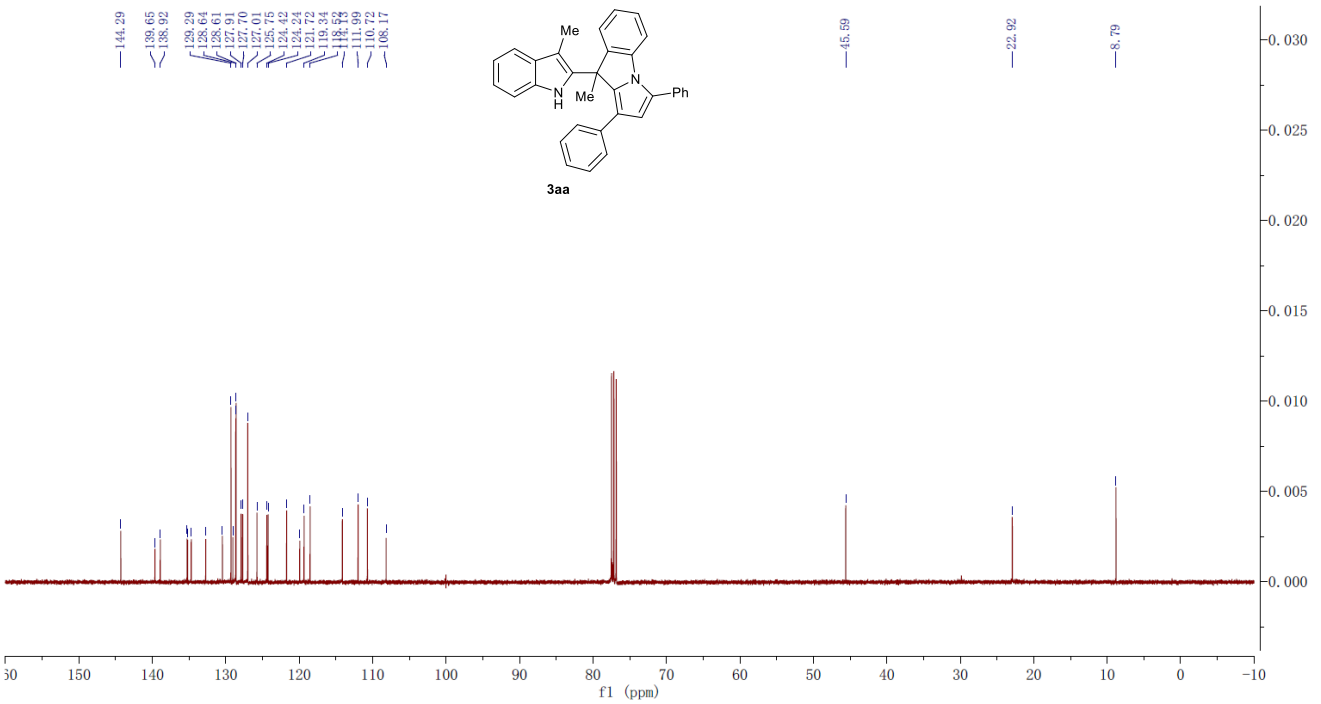
3aa, CCDC: 1944343

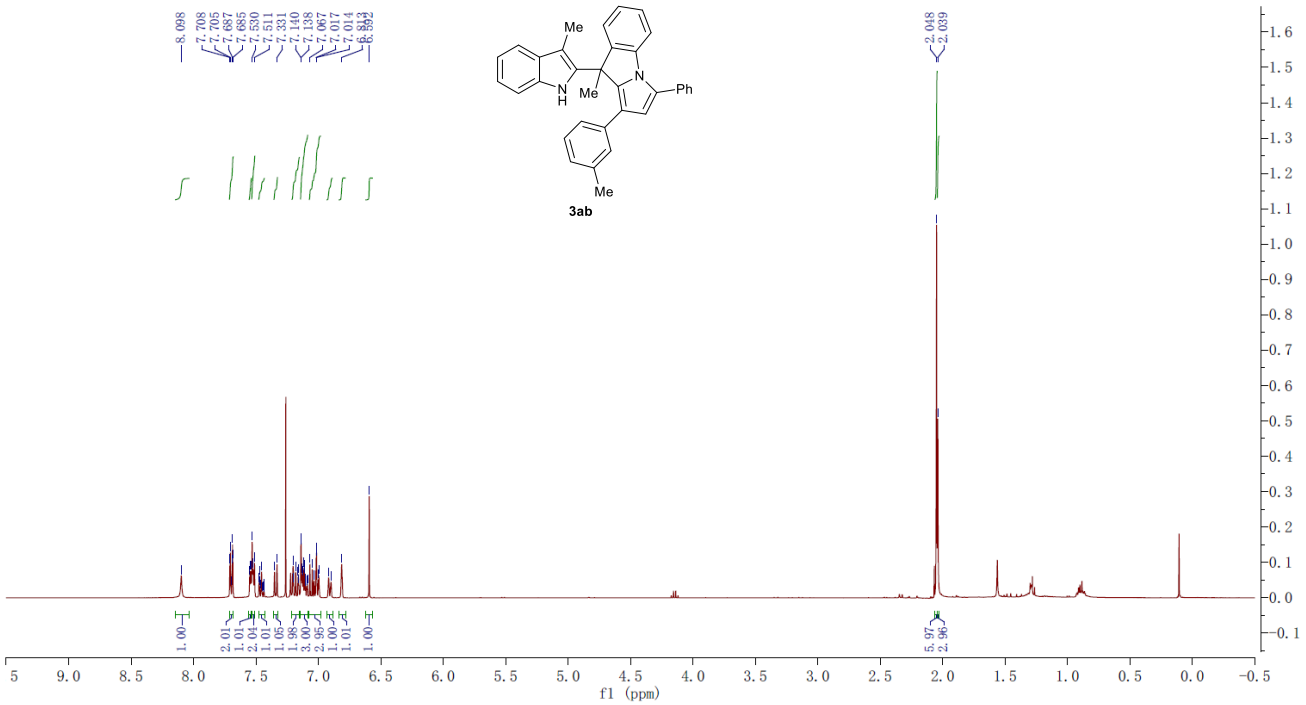
Empirical formula	$C_{33}H_{26}N_2$
Formula weight	450.56
Temperature/K	293(2)
Crystal system	N/A
Space group	C2/c
a/Å	16.9959(6)
b/Å	10.4193(4)
c/Å	30.6729(11)
α/°	90.00
β/°	90.081(3)
γ/°	90.00
Volume/Å^3	5431.7(3)
Z	8
ρ_{calc}g/cm^3	1.102
μ/mm^{-1}	0.490
F(000)	1904.0
Crystal size/mm^3	0.12 × 0.11 × 0.11
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	9.96 to 134.5
Index ranges	-18 ≤ h ≤ 20, -12 ≤ k ≤ 12, -36 ≤ l ≤ 36
Reflections collected	22454
Independent reflections	4863 [R_{int} = 0.0477, R_{sigma} = N/A]
Data/restraints/parameters	4863/0/319
Goodness-of-fit on F^2	1.499

Final R indexes [I>=2σ (I)]	R_1 = 0.1324, wR_2 = 0.3673
Final R indexes [all data]	R_1 = 0.1568, wR_2 = 0.3965
Largest diff. peak/hole / e Å^{-3}	2.96/-0.39

7. NMR Spectra



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7.014
6.592
6.592
2.048
2.039
Me
N
H
Me
N
Ph
Me
3ab
1.00
2.01
1.01
2.04
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1.65
1.98
3.05
2.00
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1.00
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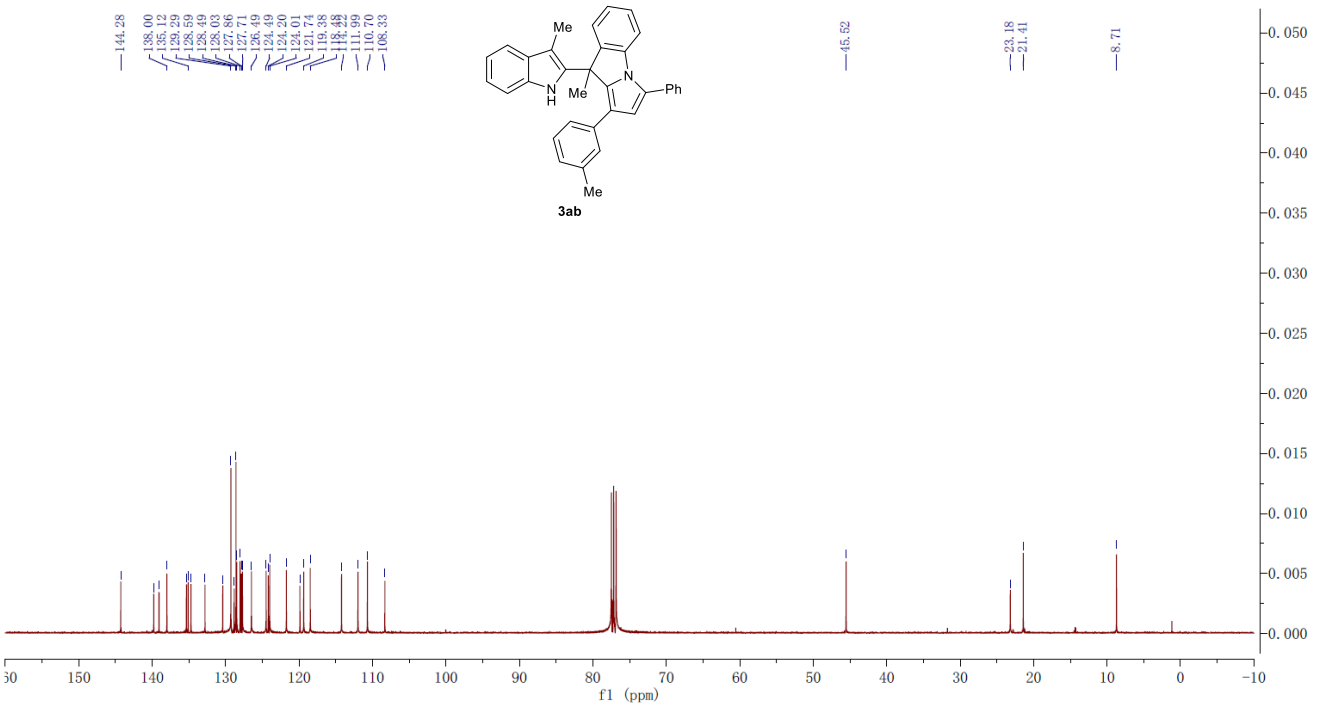
2.96
f1 (ppm)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124.01
121.74
119.38
118.45
118.41
111.99
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8.71
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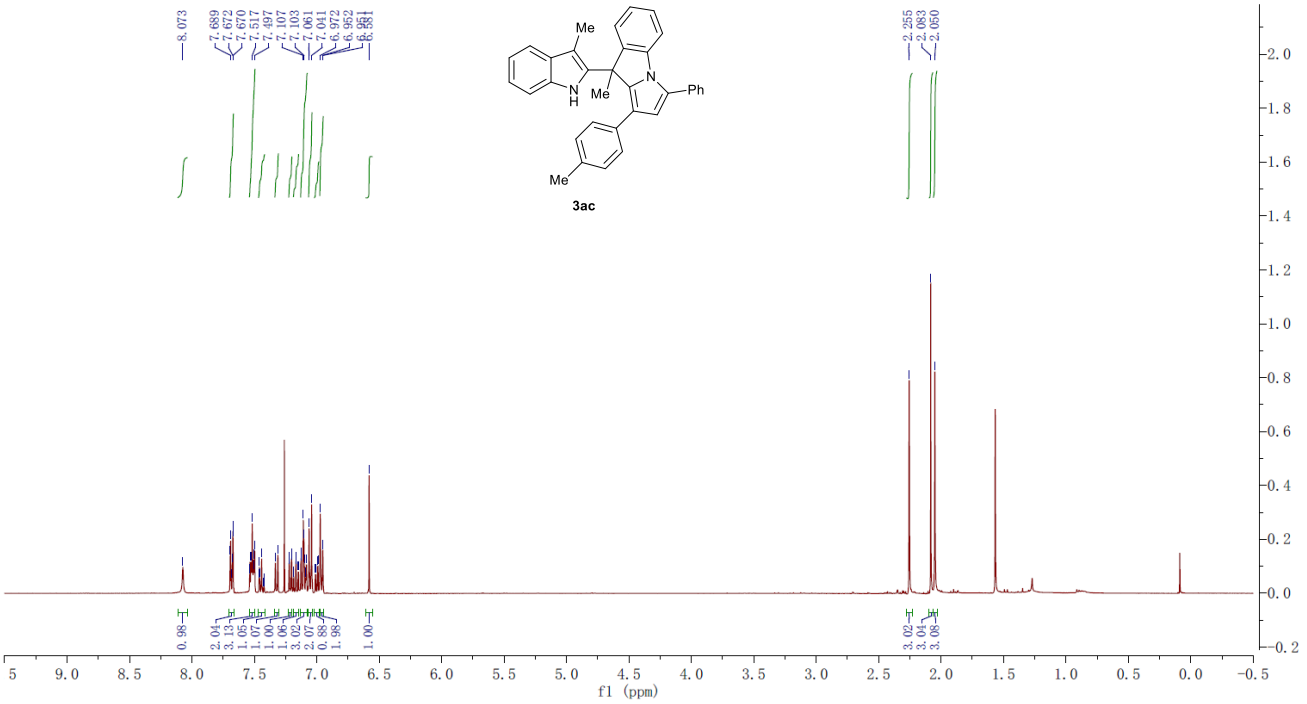
H
Me
N
Ph
Me
3ab
f1 (ppm)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2.255
2.083
2.050
Me
N
H
Me
N
Ph
Me
3ac
0.98
2.04
3.13
1.05
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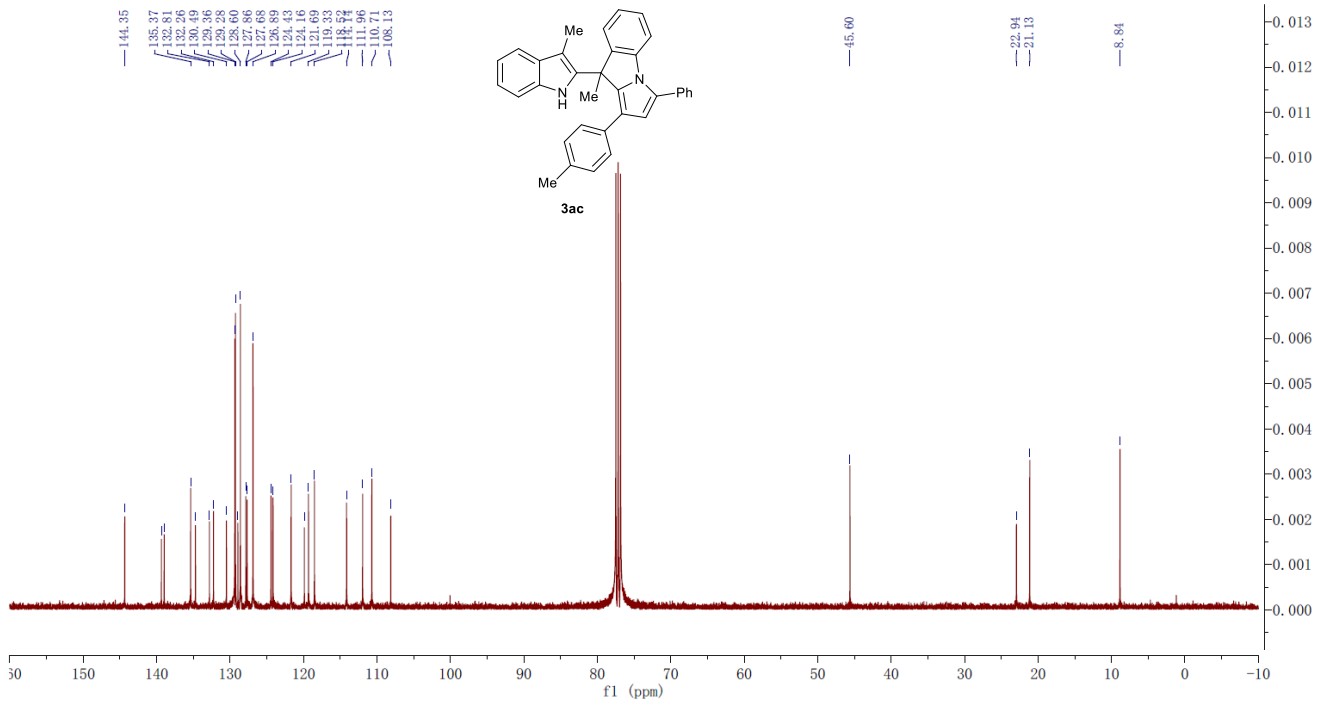
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Me
N
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Me
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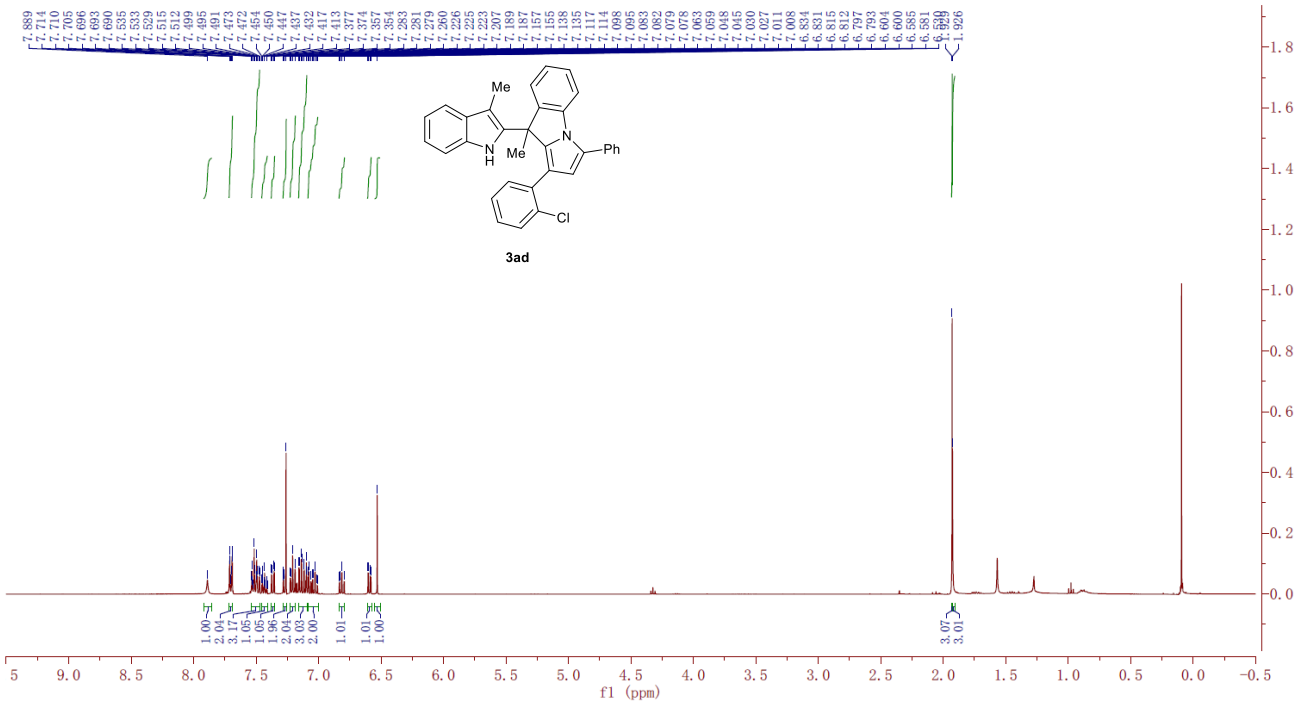
f1 (ppm)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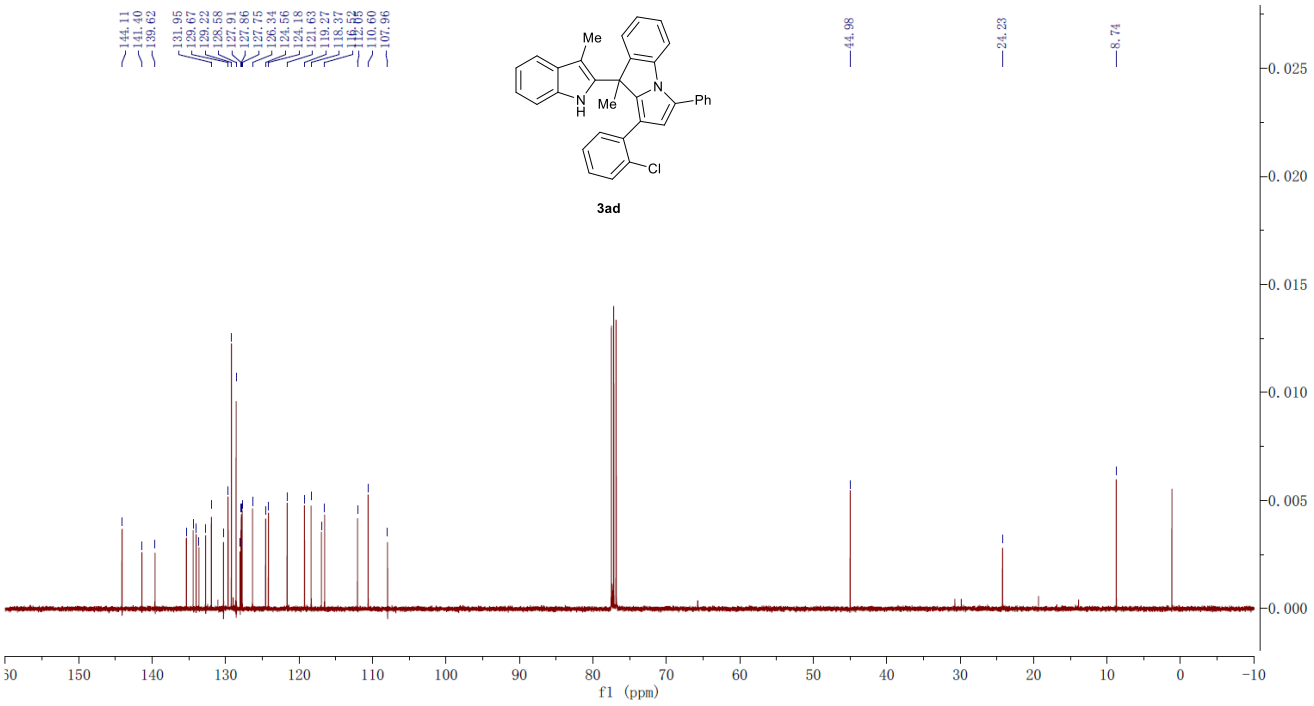
H
Me
N
Ph
Cl
3ad
f1 (ppm)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H
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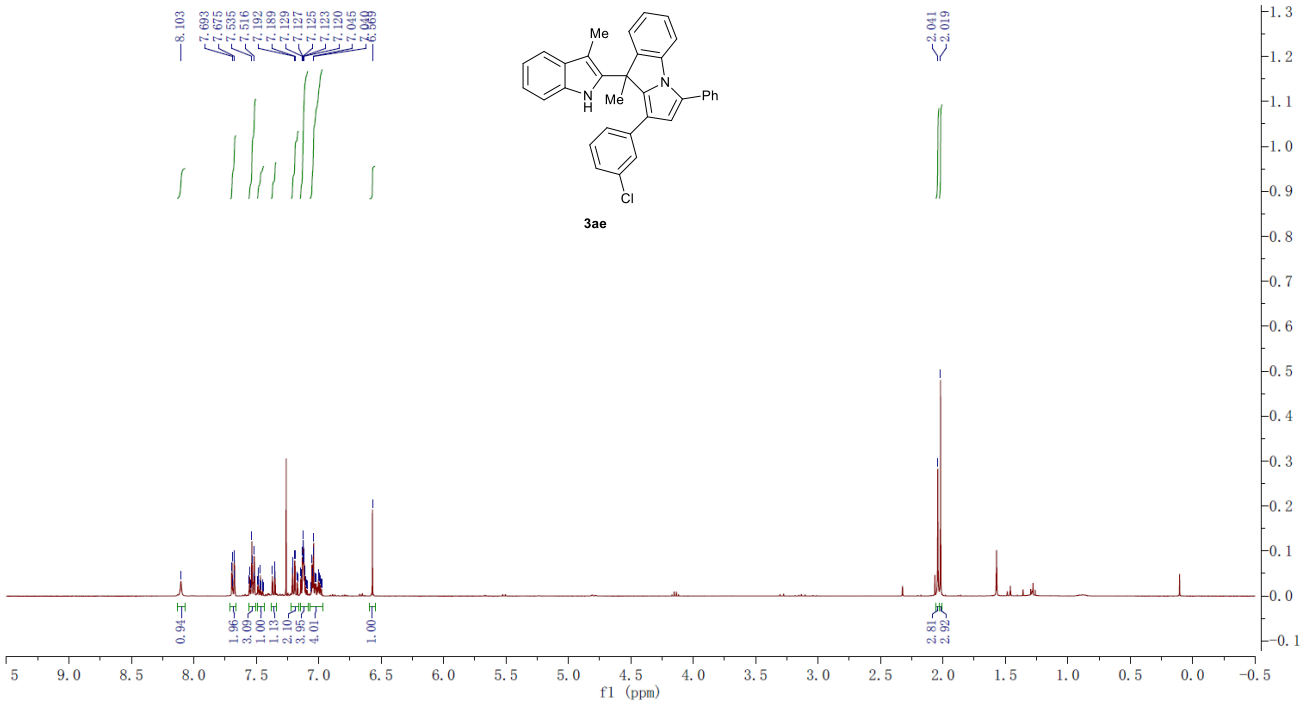
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2.019
Me
Me
N
H
N
Ph
Cl
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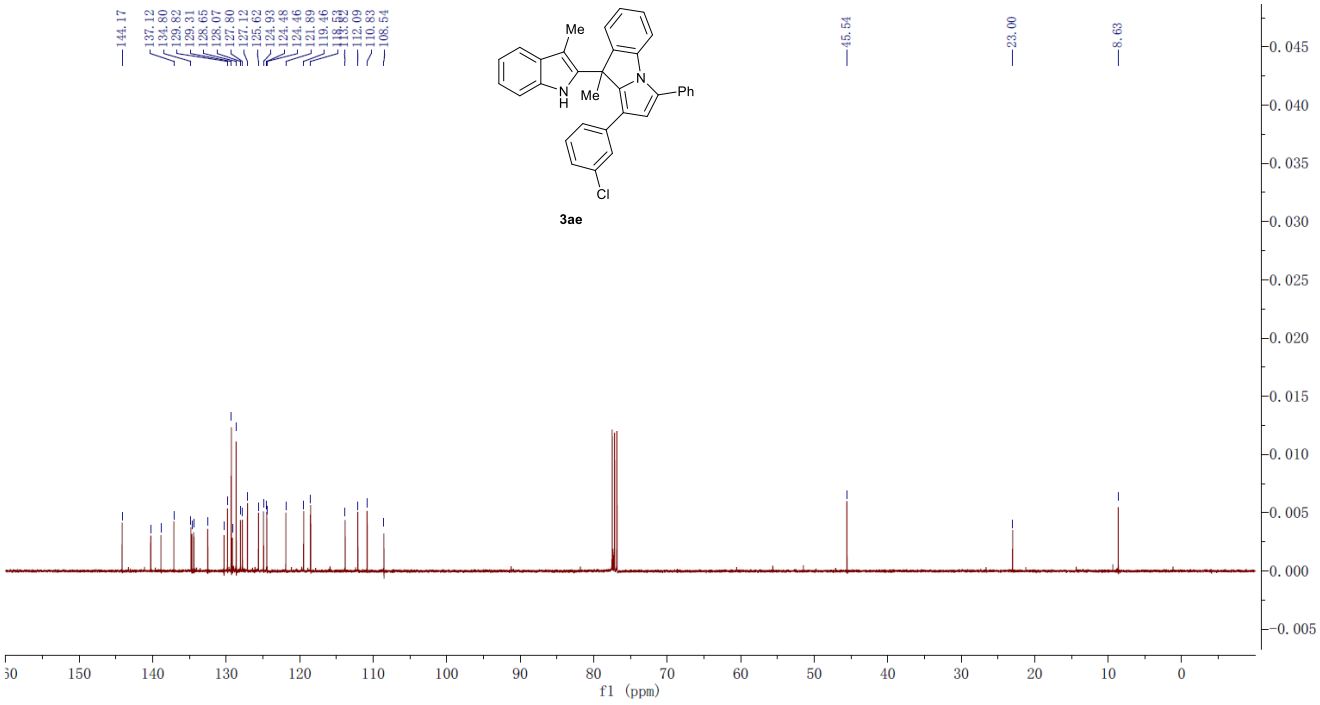
f1 (ppm)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121.69
119.46
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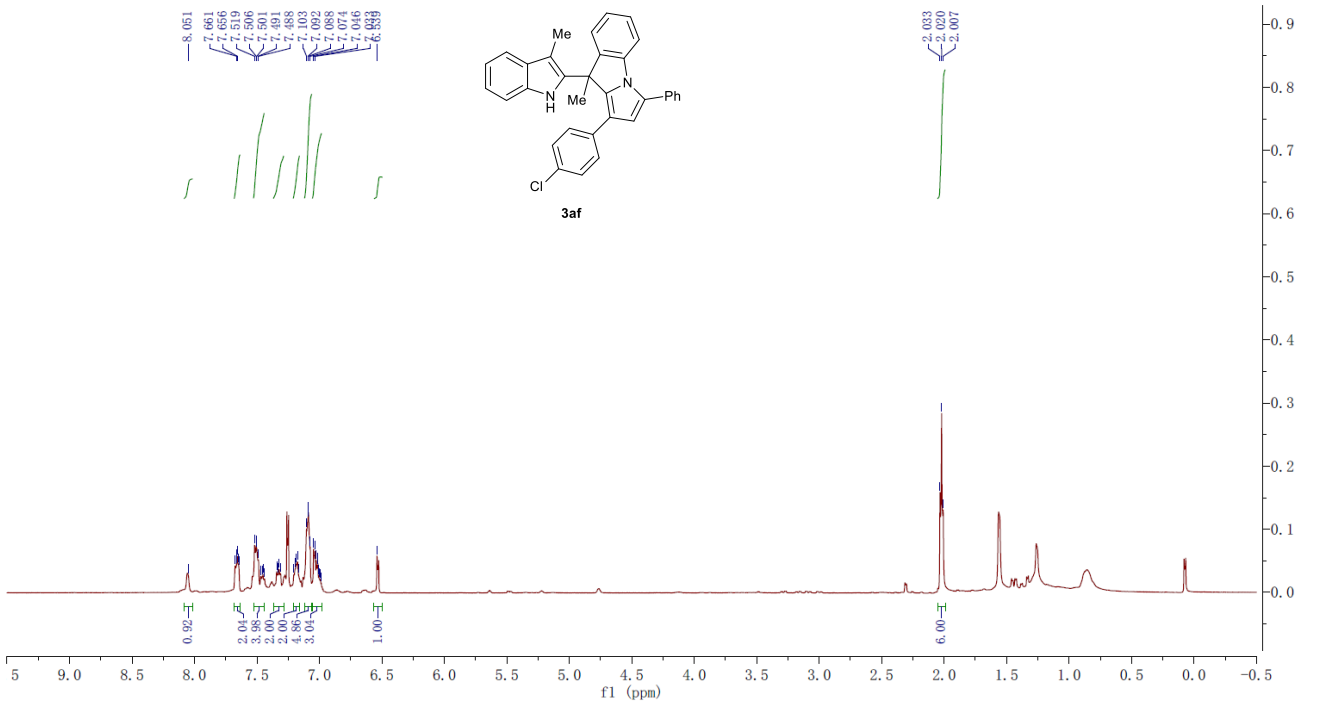
H
N
Ph
Cl
3ae
f1 (ppm)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2.020
2.007
Me
N
H
Me
N
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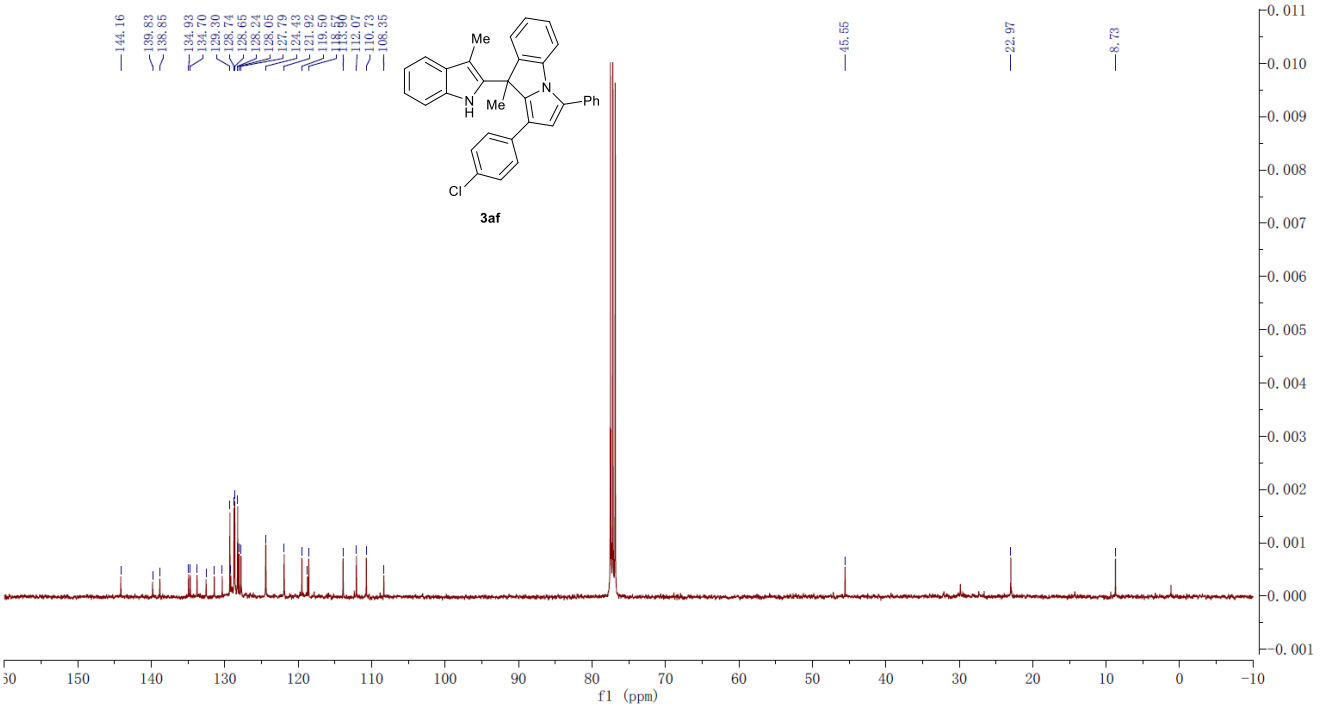
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N
Ph
Cl
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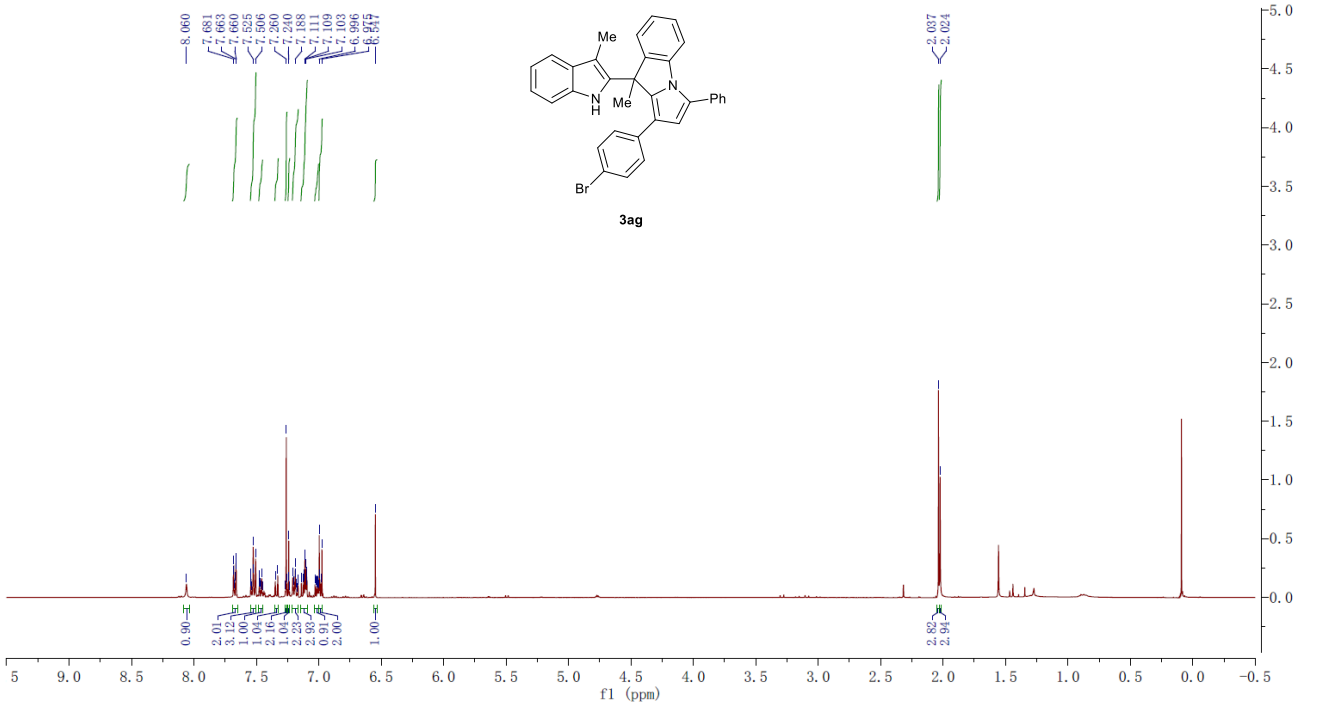
f1 (ppm)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Ph
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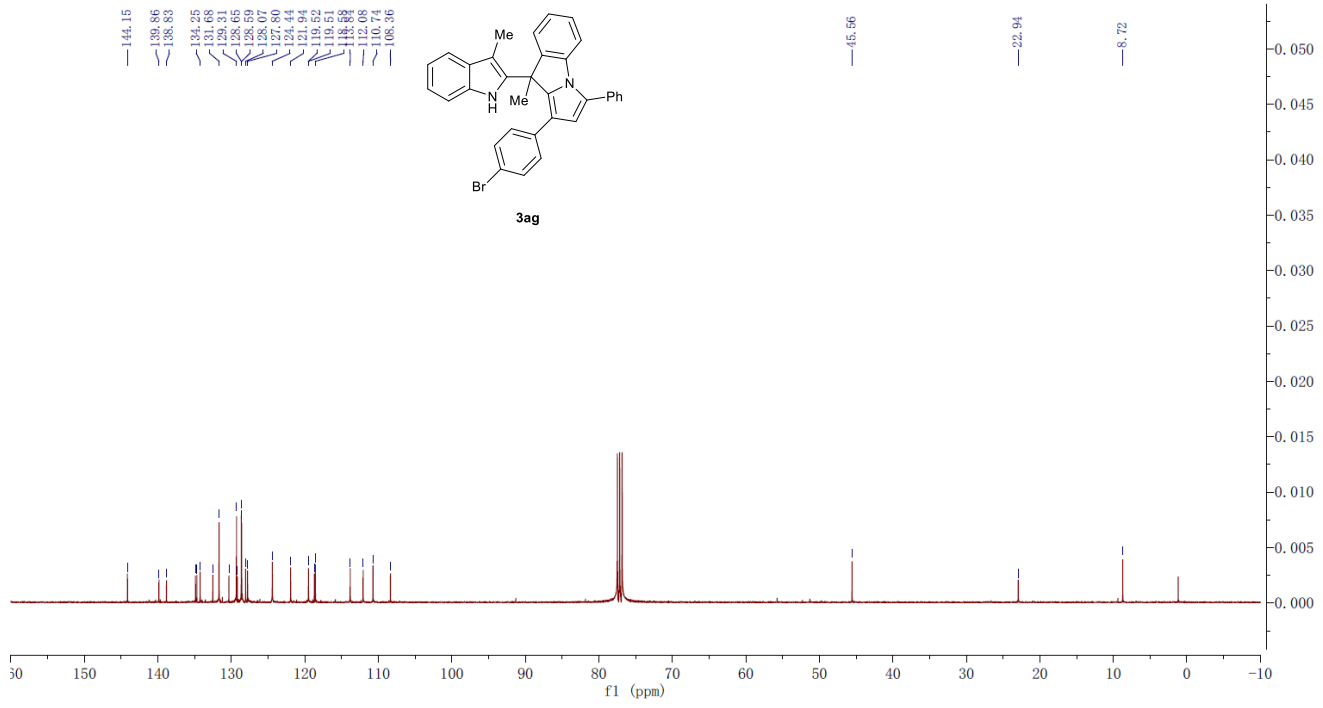
f1 (ppm)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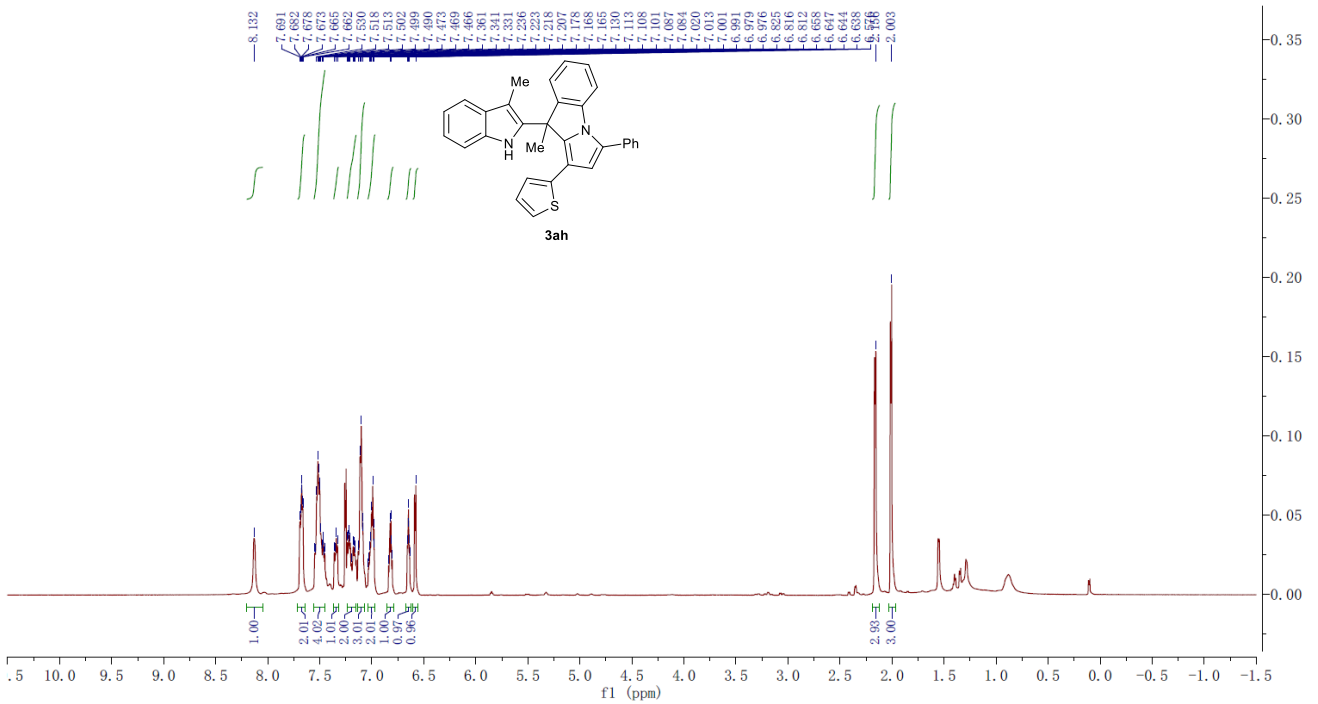
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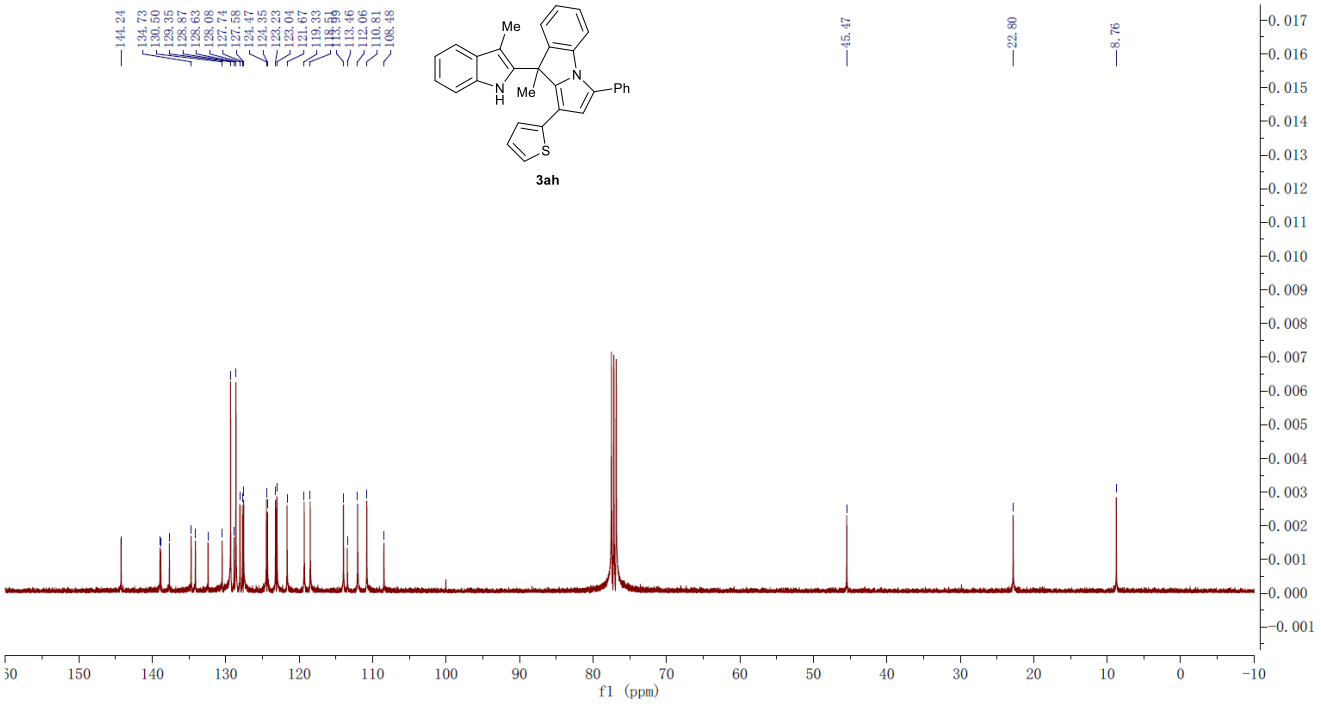
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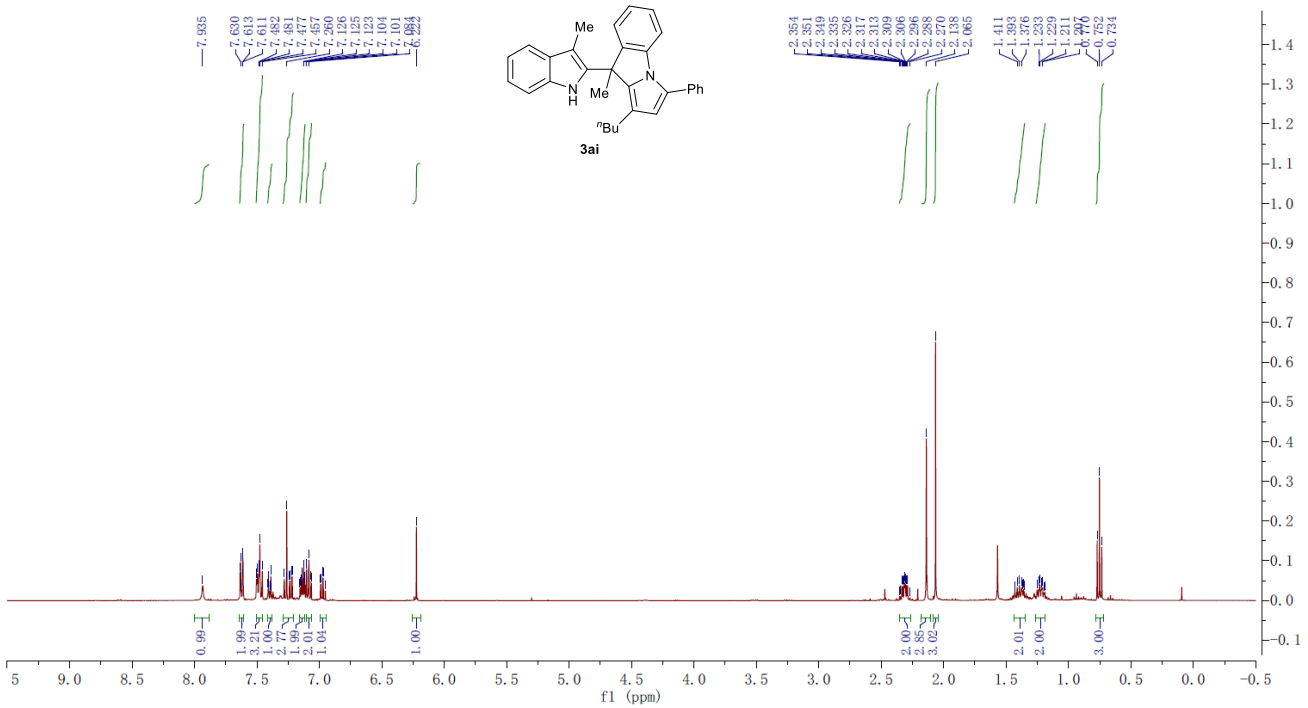
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2.349
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2.326
2.317
2.313
2.309
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2.288
2.270
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2.065
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1.393
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1.229
1.211
0.775
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0.734
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Me
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H
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Ph
nBu
3ai
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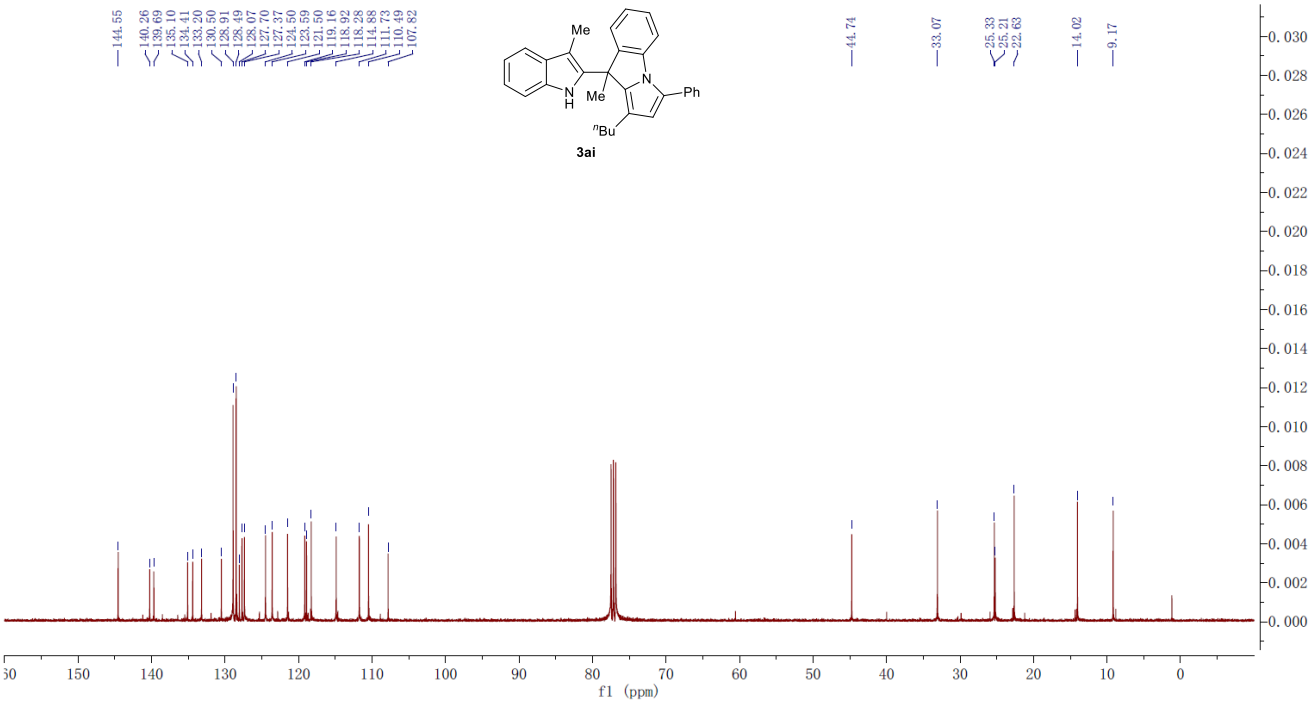
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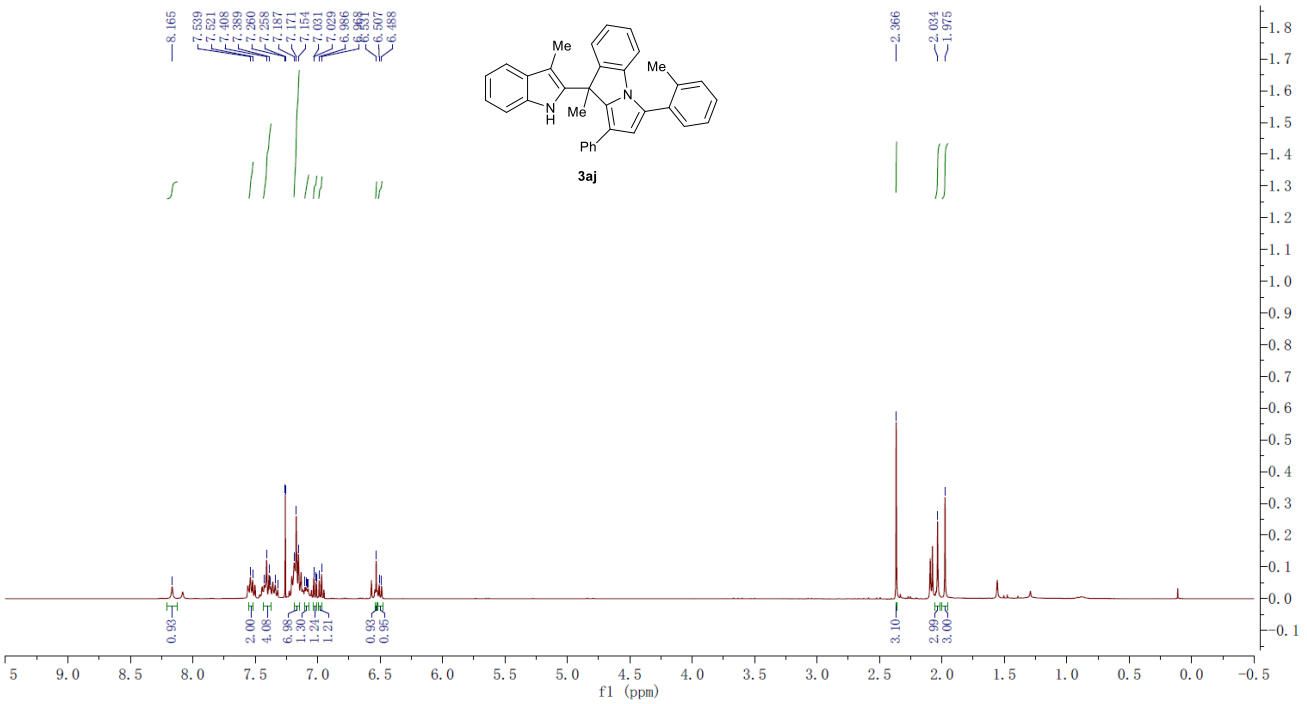
f1 (ppm)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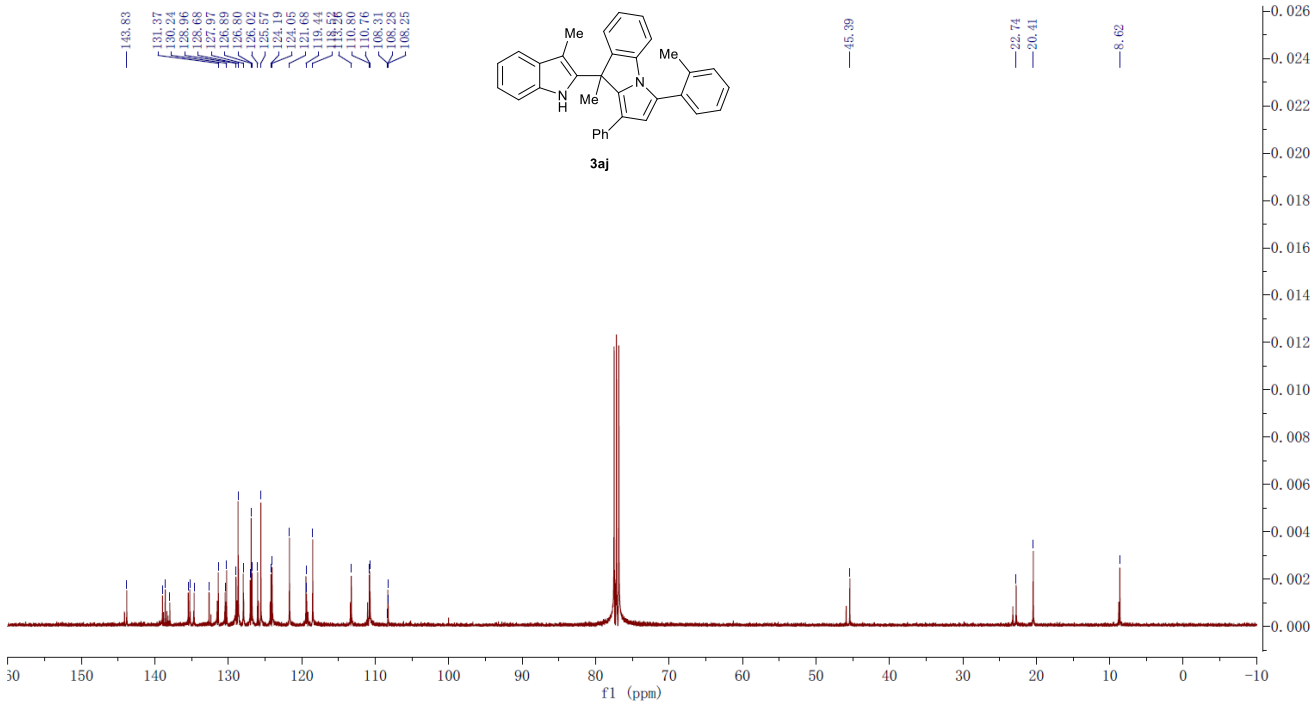
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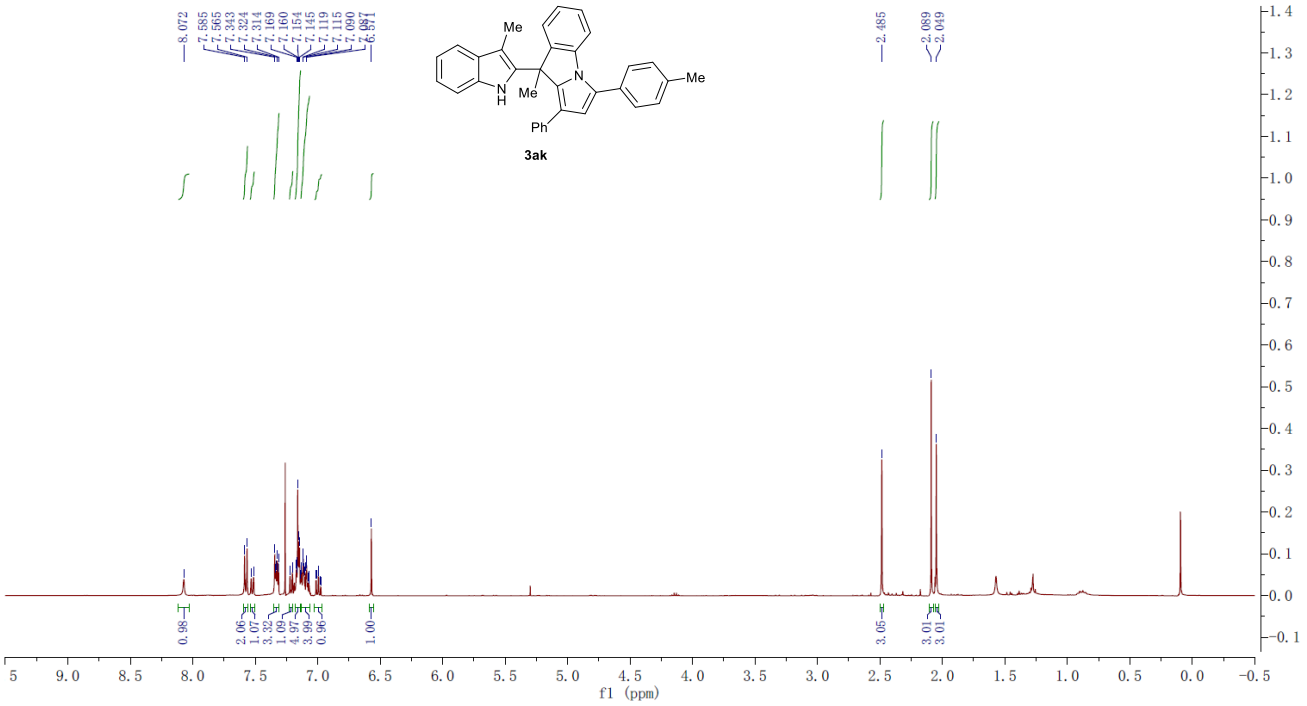
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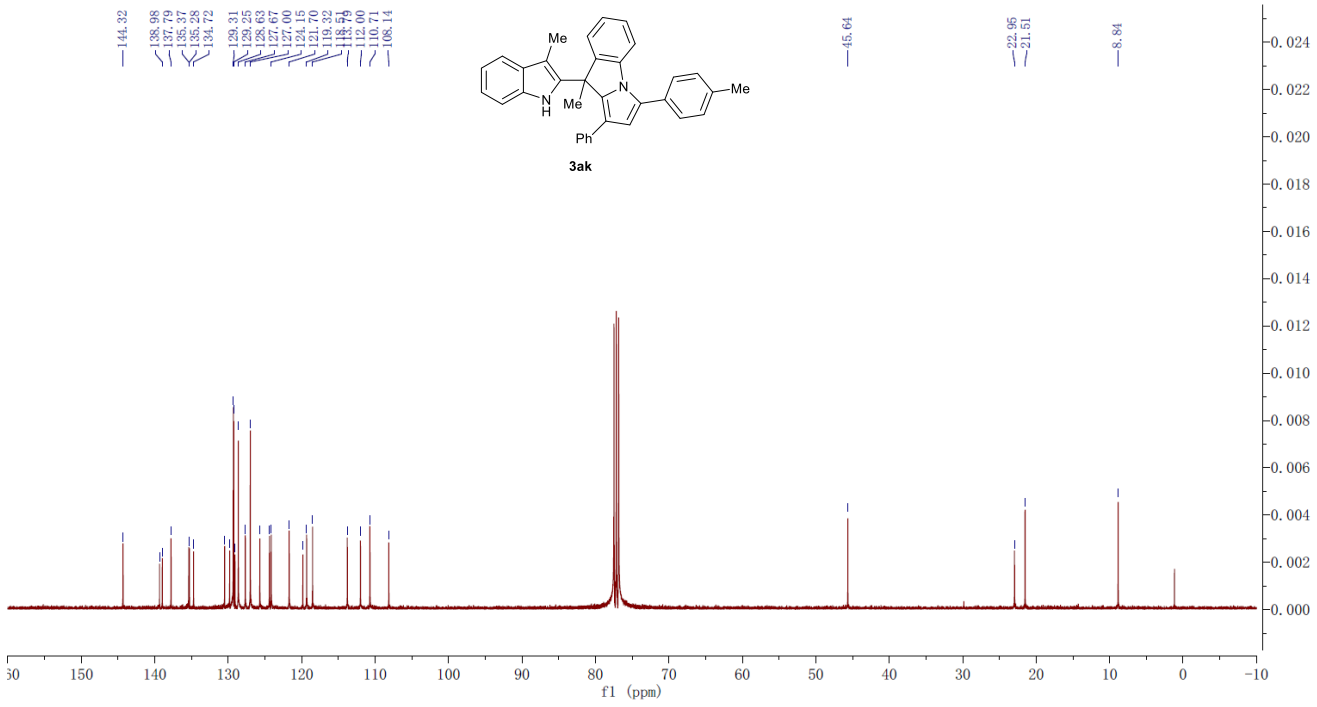
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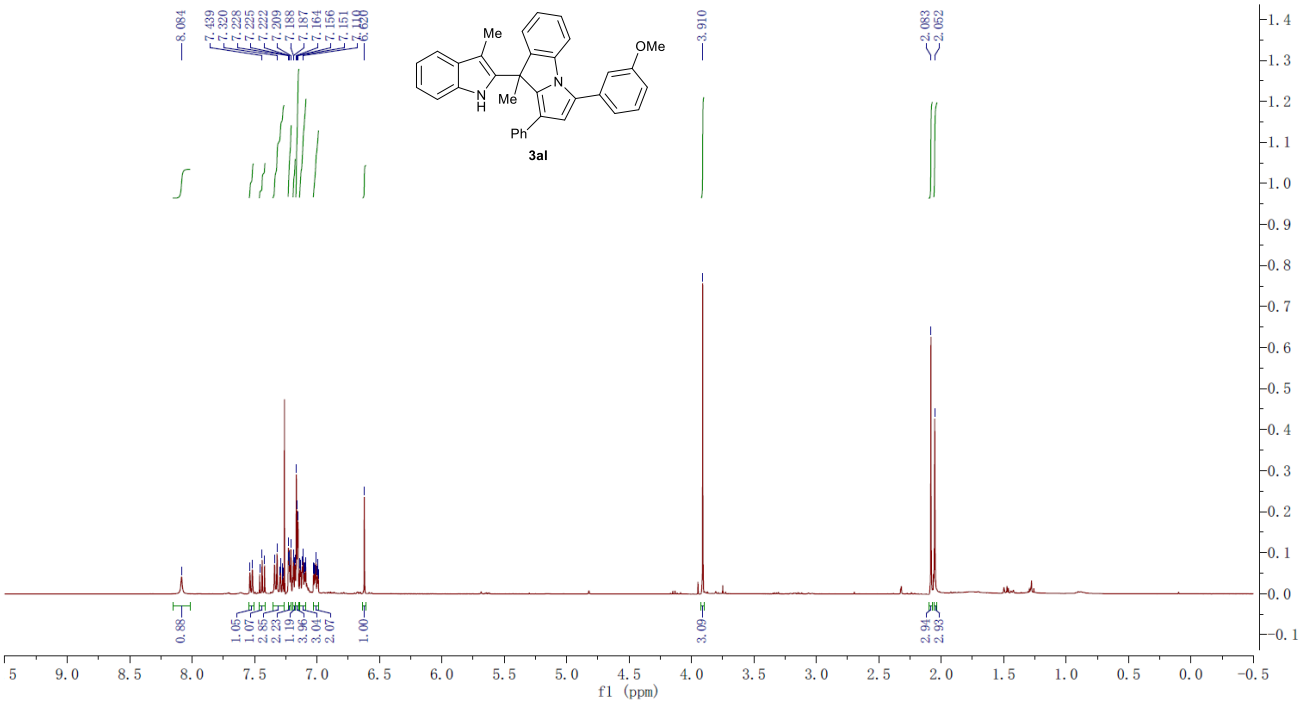
f1 (ppm)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OMe
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Me
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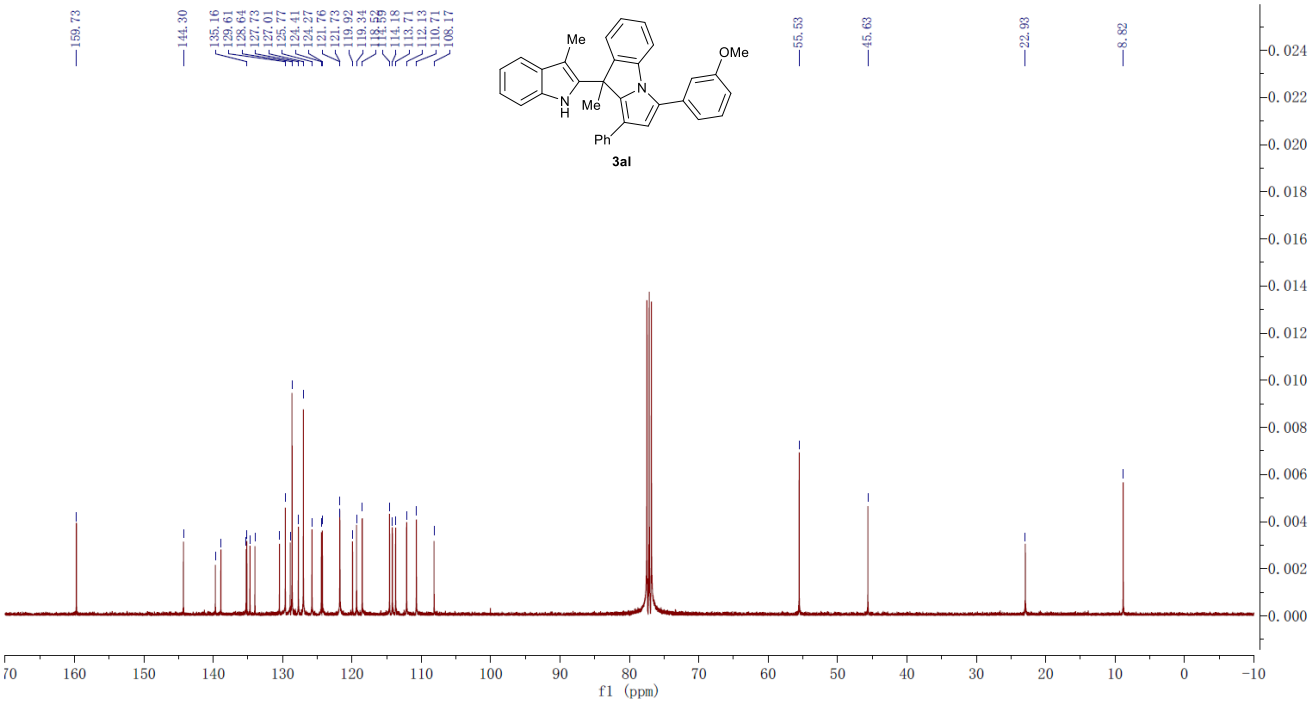
f1 (ppm)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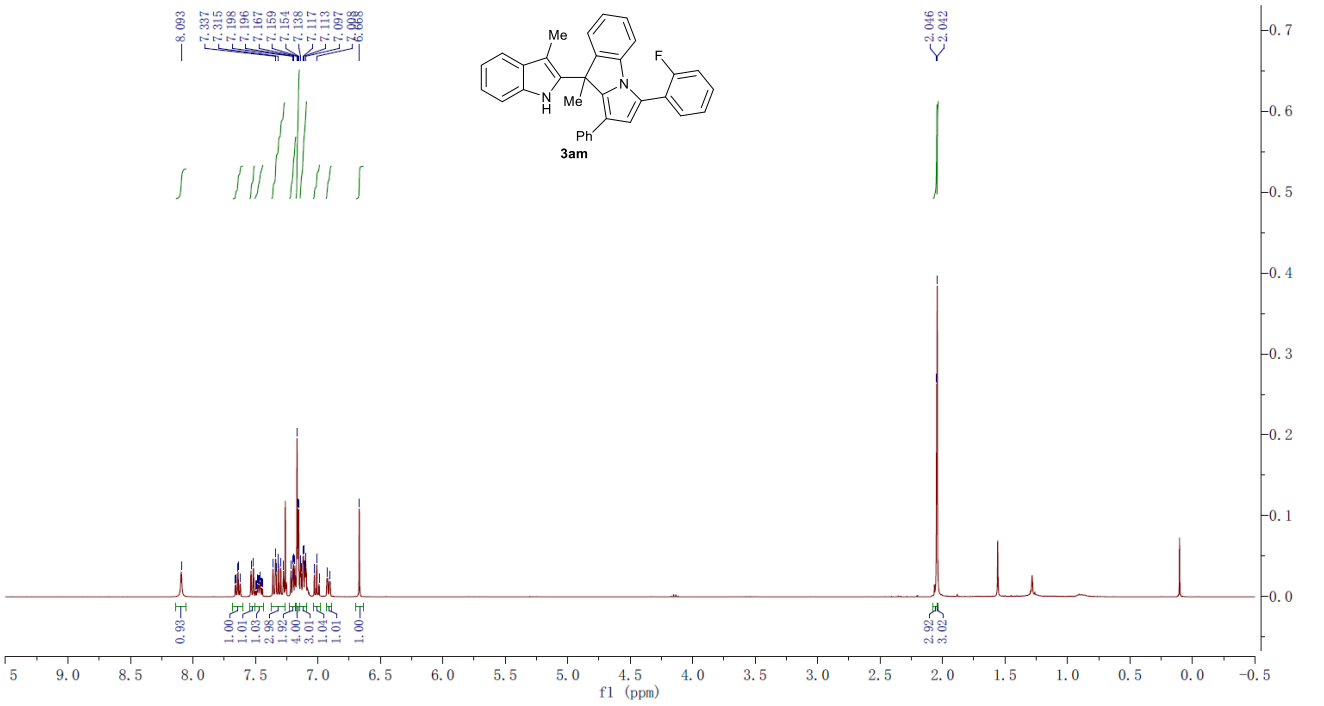
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Me
F
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H
Ph
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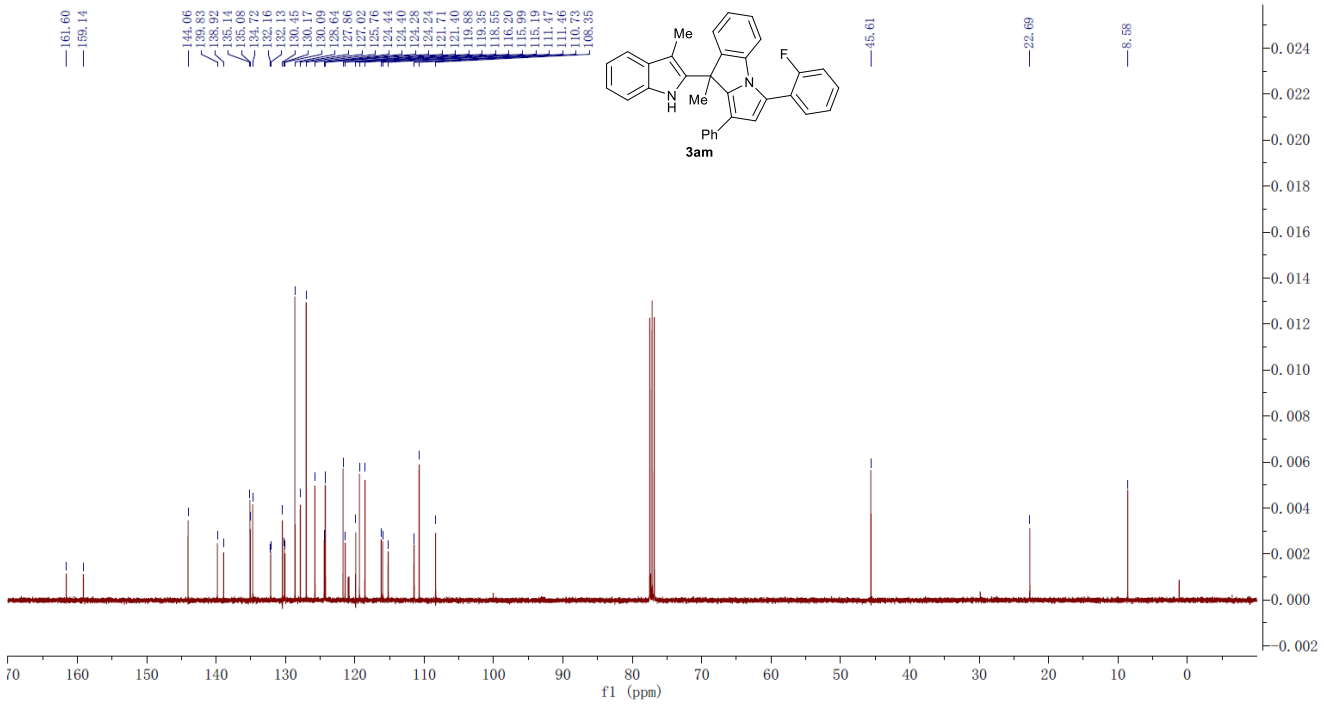
f1 (ppm)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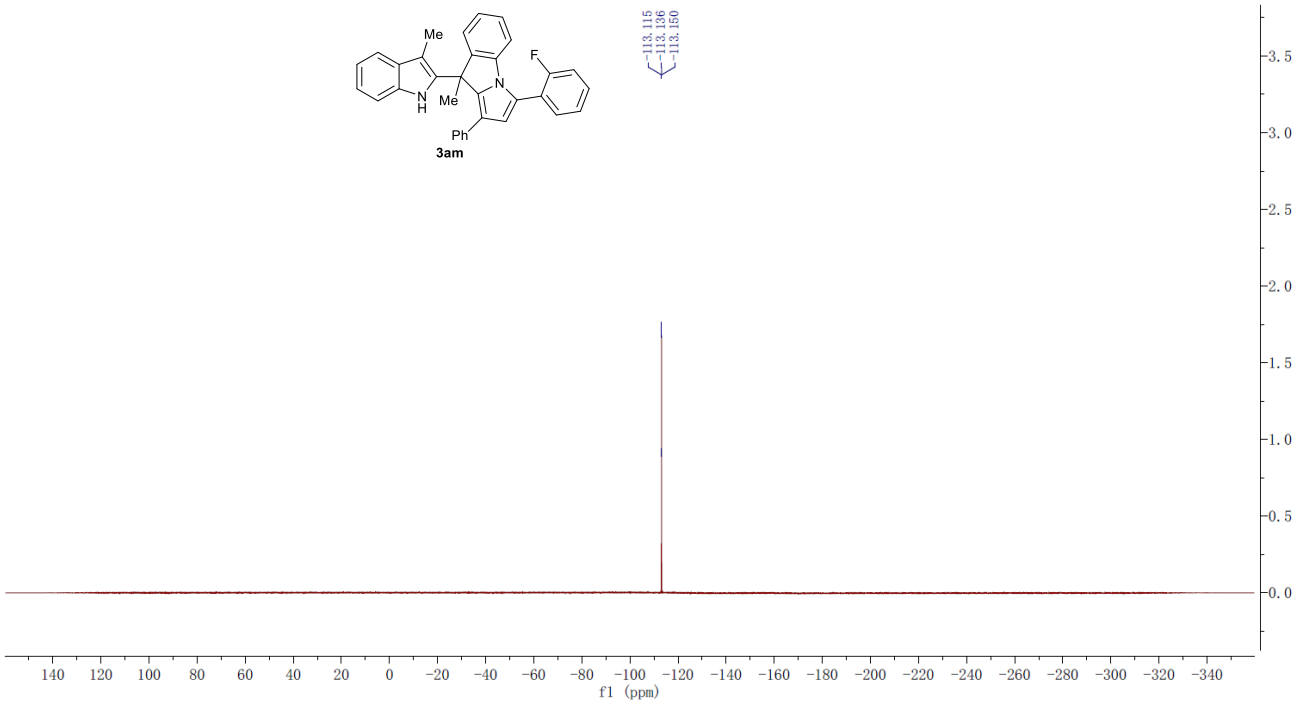
f1 (ppm)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1.5
1.0
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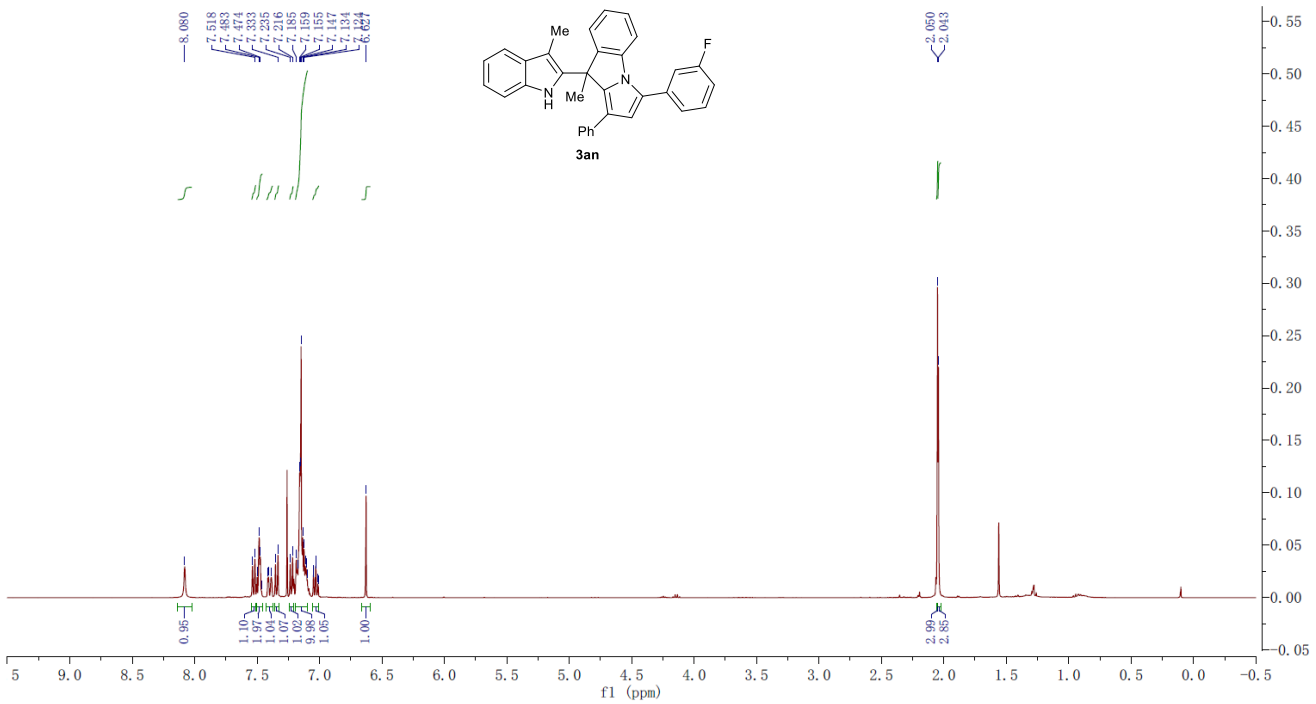
f1 (ppm)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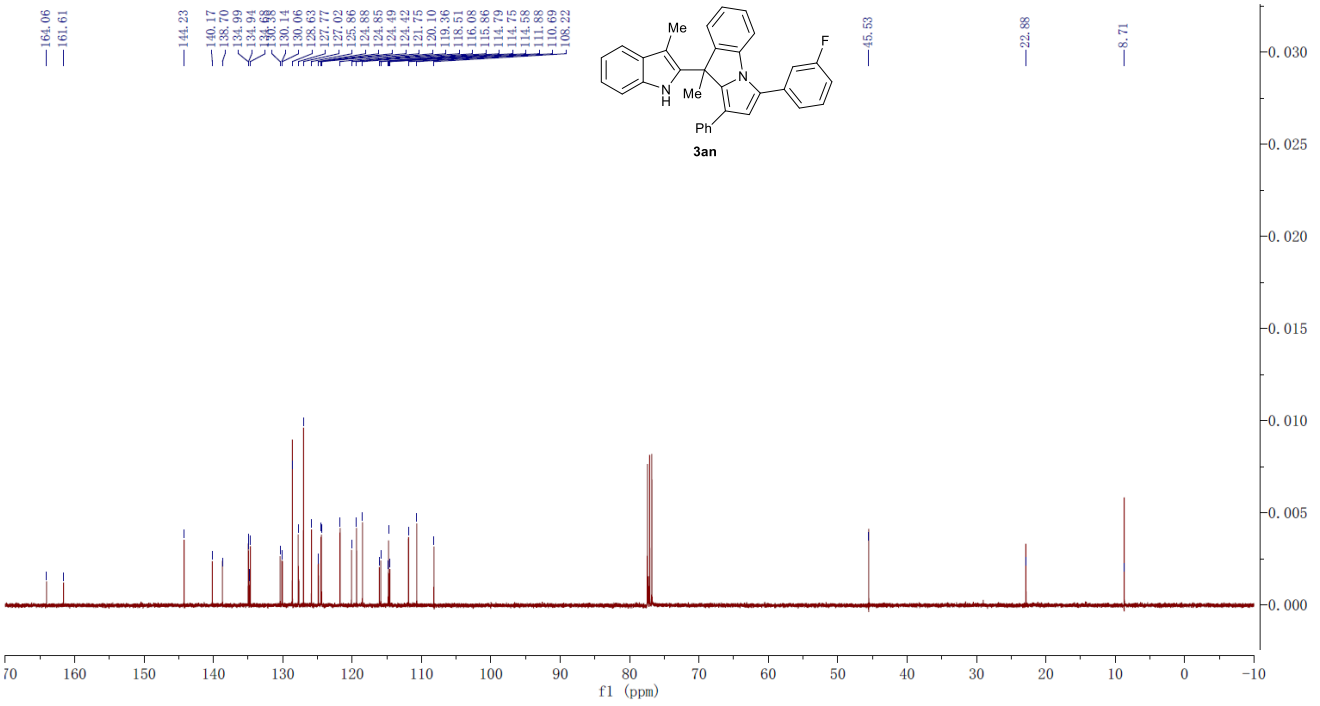
7.483
7.474
7.333
7.235
7.216
7.185
7.159
7.155
7.147
7.134
7.124
6.624
2.050
2.043
Me
Me
Ph
F
N
H
3an
0.96
1.10
1.97
1.04
1.07
1.02
9.98
1.05
1.00
2.99
2.85
f1 (ppm)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161.61
144.23
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134.99
134.94
130.14
130.06
128.63
127.77
127.02
125.86
124.88
124.85
124.49
124.42
121.75
120.10
119.36
118.51
116.08
115.86
114.79
114.75
114.58
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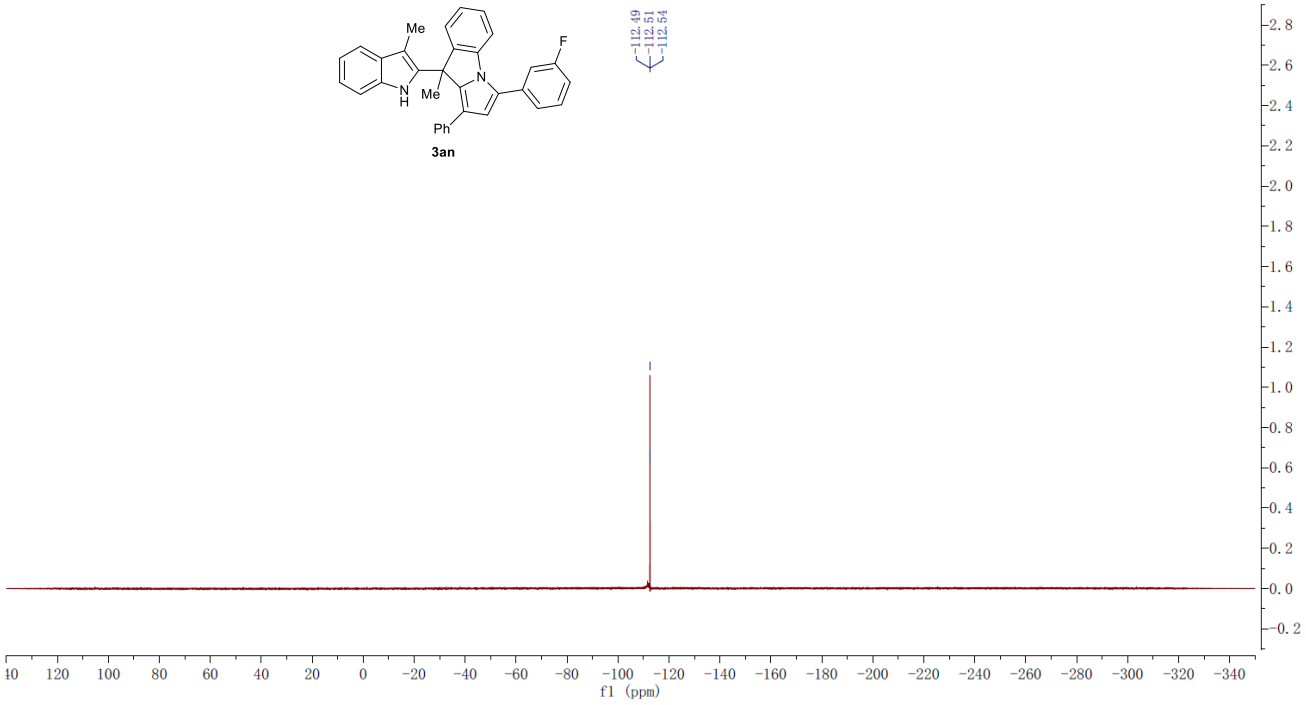
108.22
45.53
22.88
8.71
Me
Me
Ph
F
N
H
3an
f1 (ppm)


Me
N
H
Me
N
F
Ph
3an
-112.49
-112.51
-112.54
2.8
2.6
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
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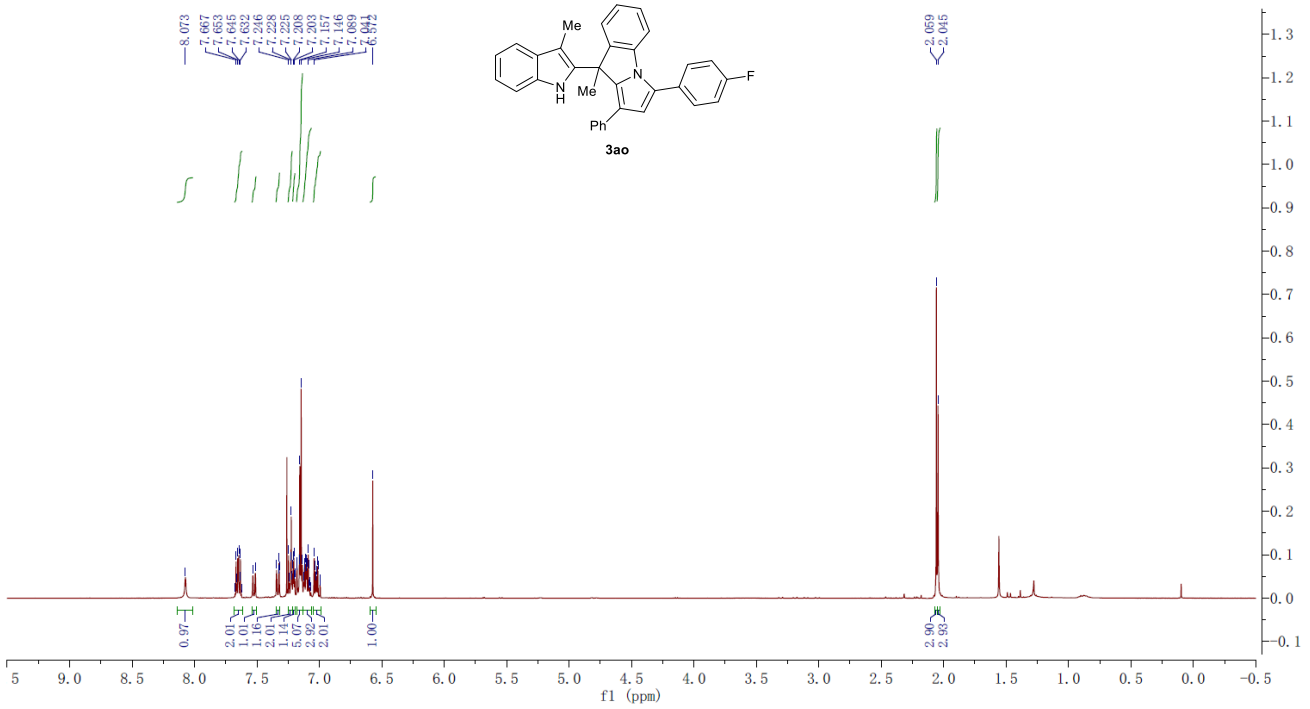
f1 (ppm)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7.632
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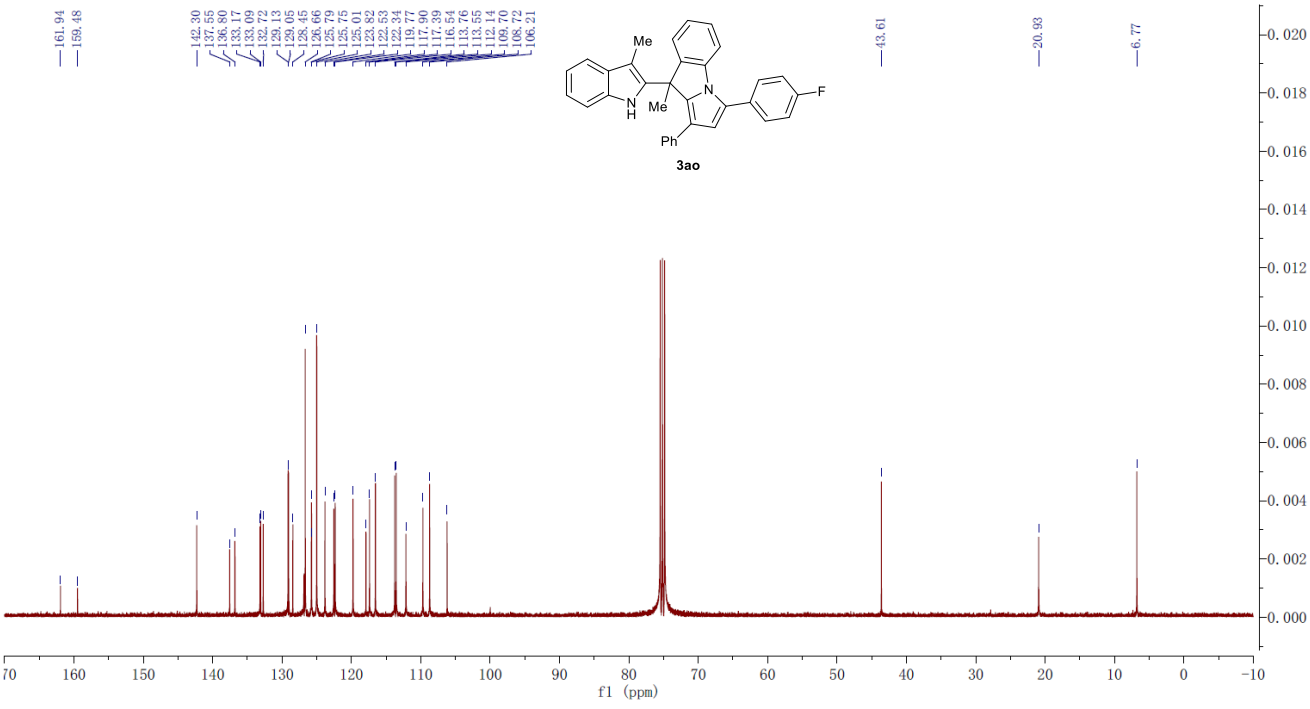
7.228
7.225
7.208
7.203
7.157
7.146
7.089
2.059
2.045
Me
Me
N
H
N
Ph
F
3ao
0.97
2.01
1.01
1.16
2.01
1.14
5.07
2.92
2.01
1.00
2.90
2.93
f1 (ppm)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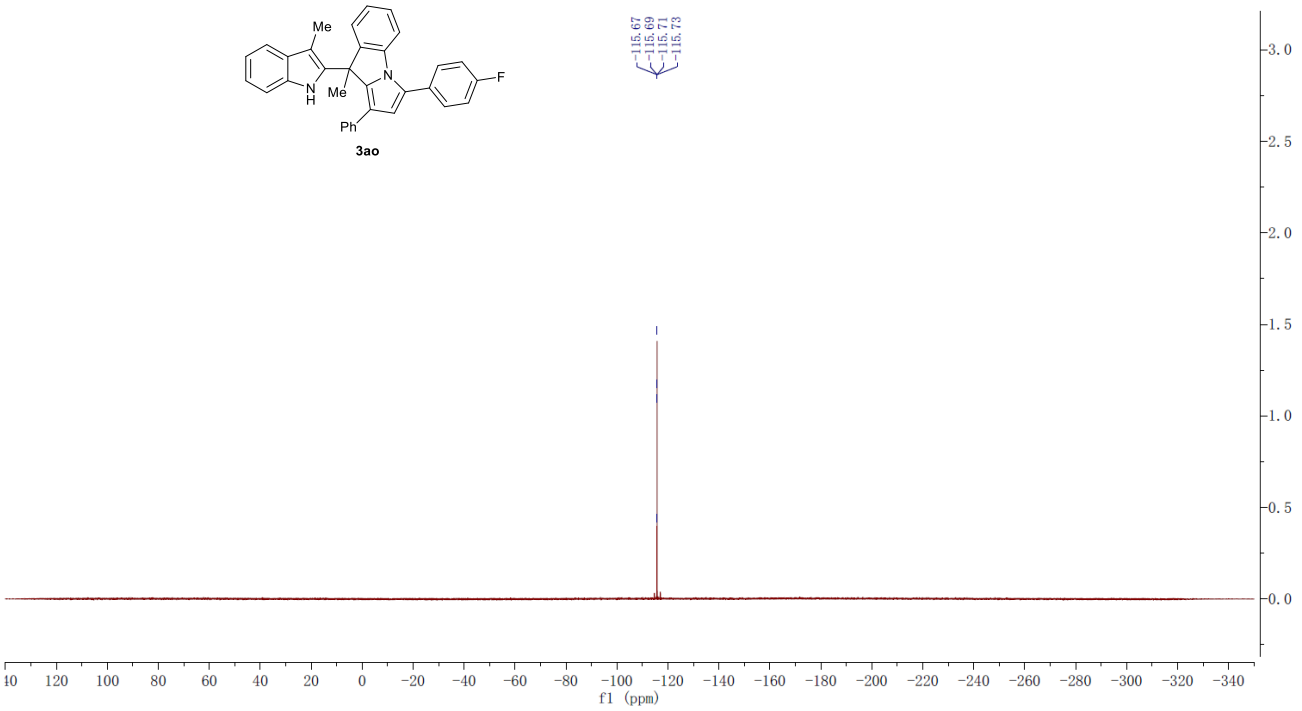
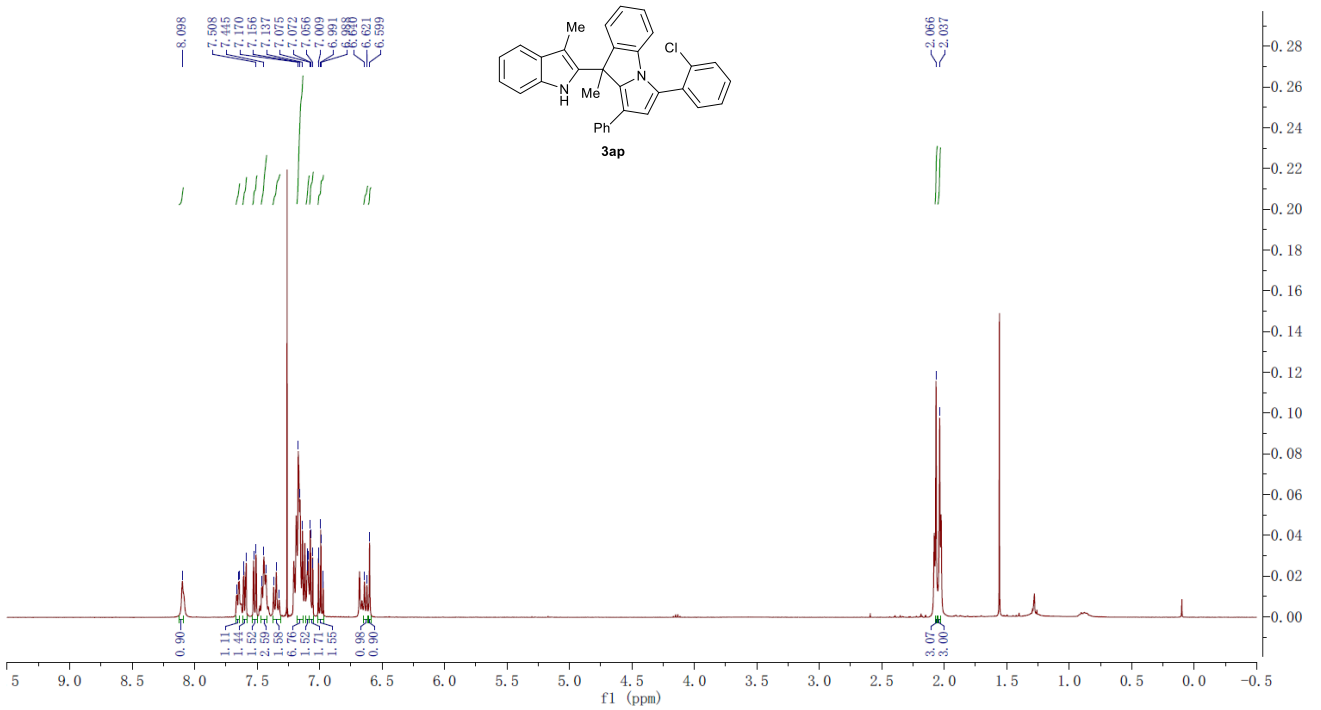
136.80
133.17
133.09
132.72
129.13
129.05
128.45
126.66
125.79
125.75
125.01
123.82
122.53
122.34
119.77
117.90
117.39
116.54
113.76
113.55
112.14
109.70
108.72
106.21
43.61
20.93
6.77
Me
Me
N
H
N
Ph
F
3ao
f1 (ppm)


Me
Me
Ph
N
H
N
F
3ao
-115.67
-115.69
-115.71
-115.73
3.0
2.5
2.0
1.5
1.0
0.5
0.0
40 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300 -320 -340
f1 (ppm)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7.508
7.445
7.170
7.156
7.137
7.075
7.072
7.056
7.009
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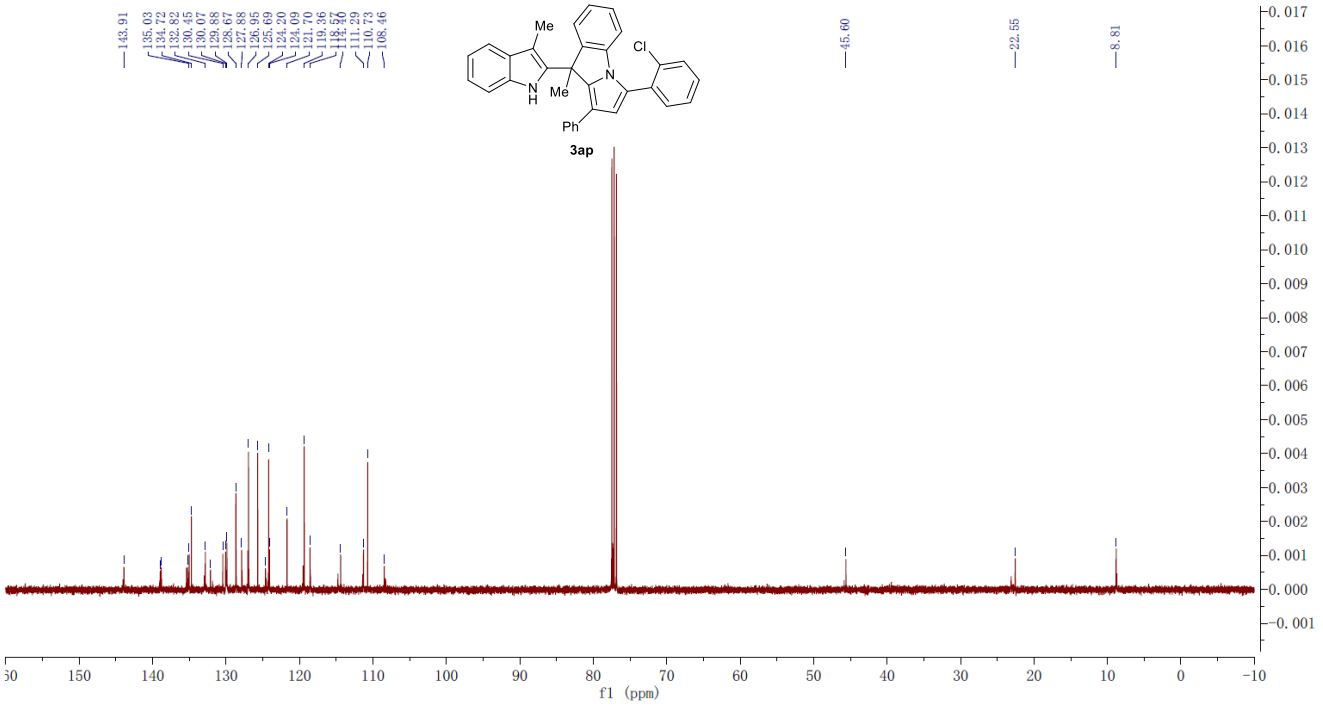
6.621
6.599
2.066
2.037
Me
Me
Cl
N
H
N
Ph
3ap
f1 (ppm)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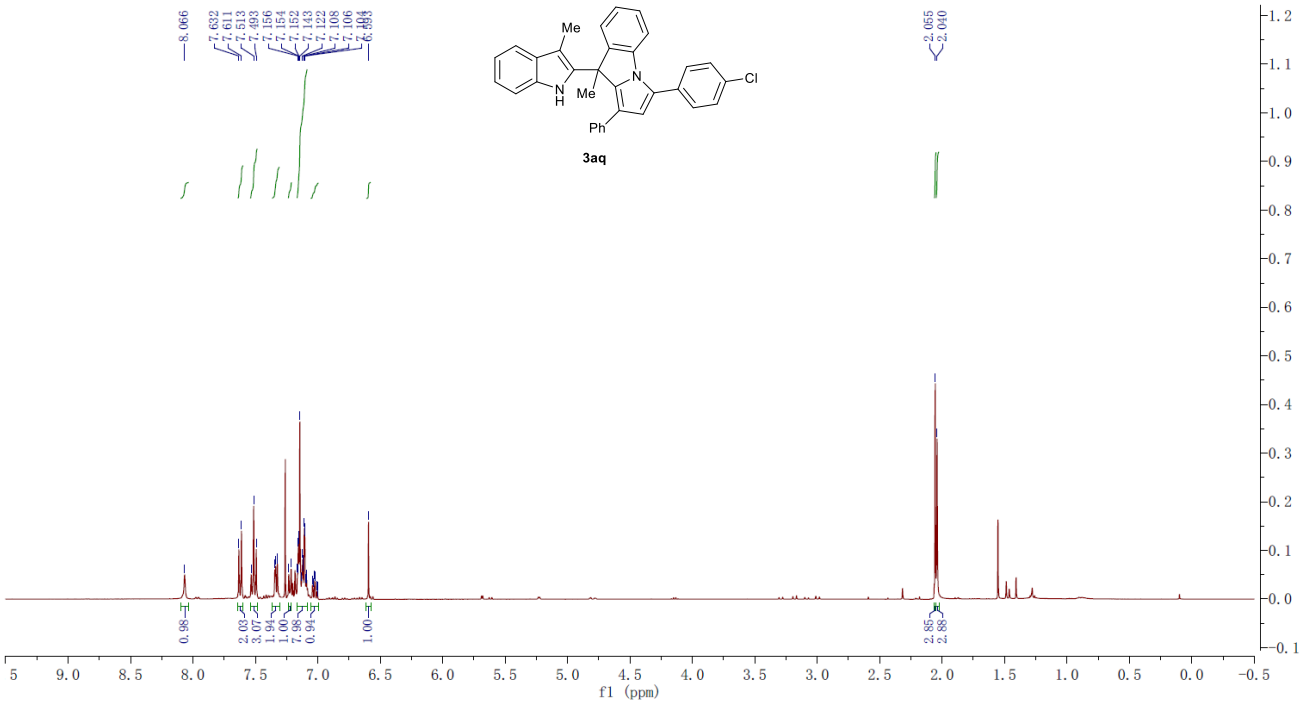
135.03
134.72
132.82
130.45
130.07
129.88
128.67
127.88
126.95
125.69
124.60
124.09
121.70
121.36
118.57
111.29
110.73
108.46
45.60
22.55
8.81
Me
Me
Cl
N
H
N
Ph
3ap
f1 (ppm)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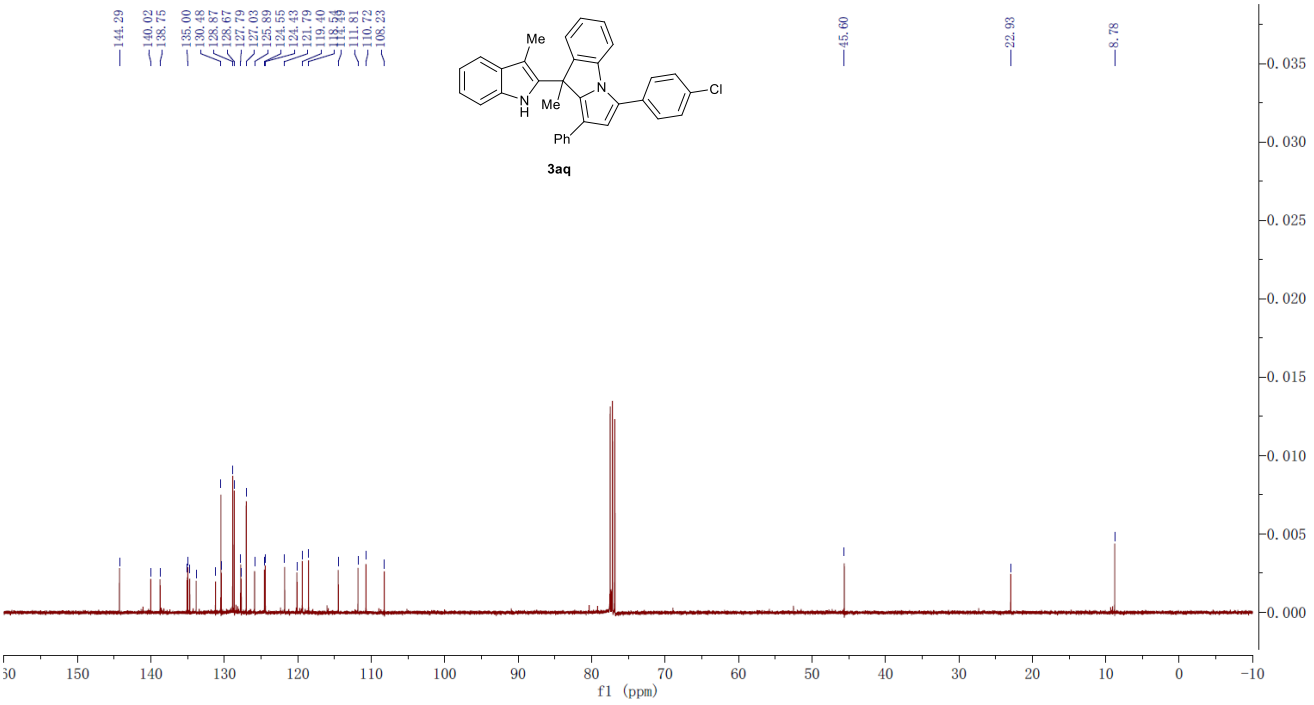
7.632
7.611
7.513
7.493
7.156
7.154
7.152
7.143
7.122
7.108
7.106
2.055
2.040
Me
Me
N
H
N
Cl
Ph
3aq
0.98
2.03
3.07
1.94
1.00
7.98
0.94
1.00
2.85
2.88
f1 (ppm)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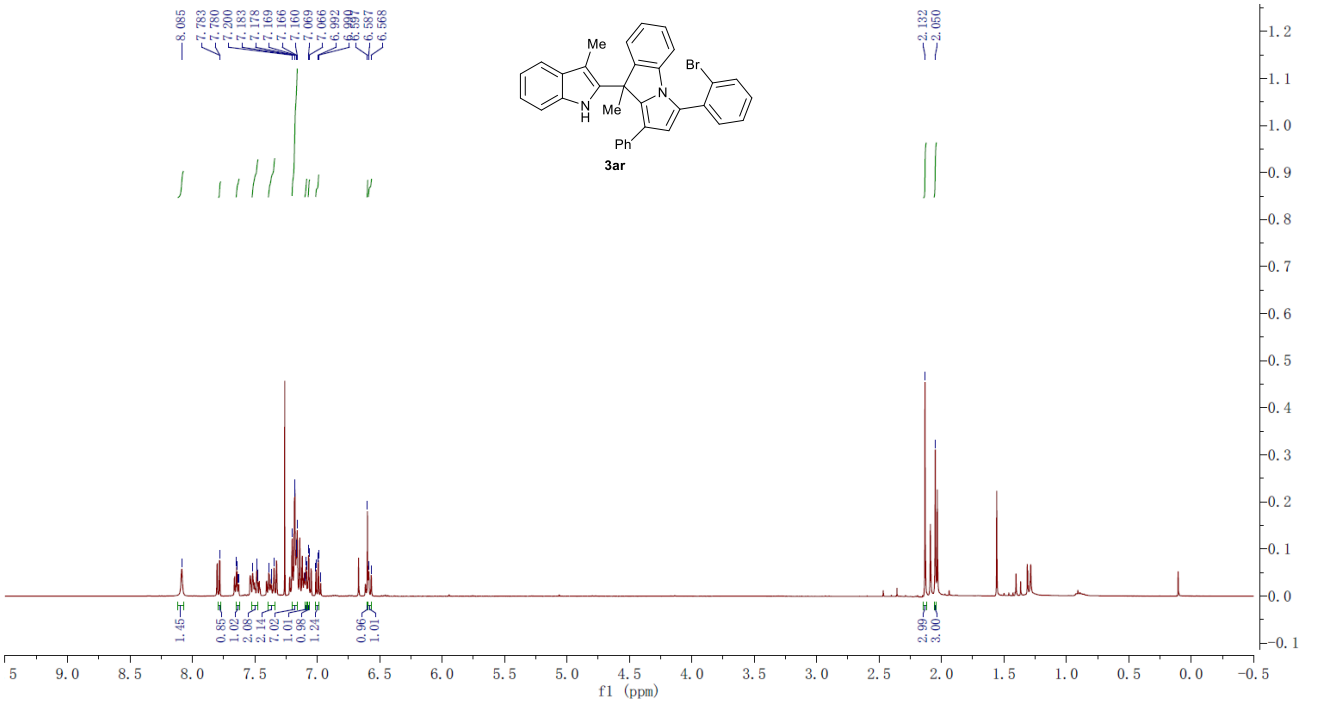
140.02
138.75
135.00
130.48
128.87
128.67
127.79
127.03
125.89
124.55
124.43
121.79
119.40
111.81
110.72
108.23
45.60
22.93
8.78
Me
Me
N
H
N
Cl
Ph
3aq
f1 (ppm)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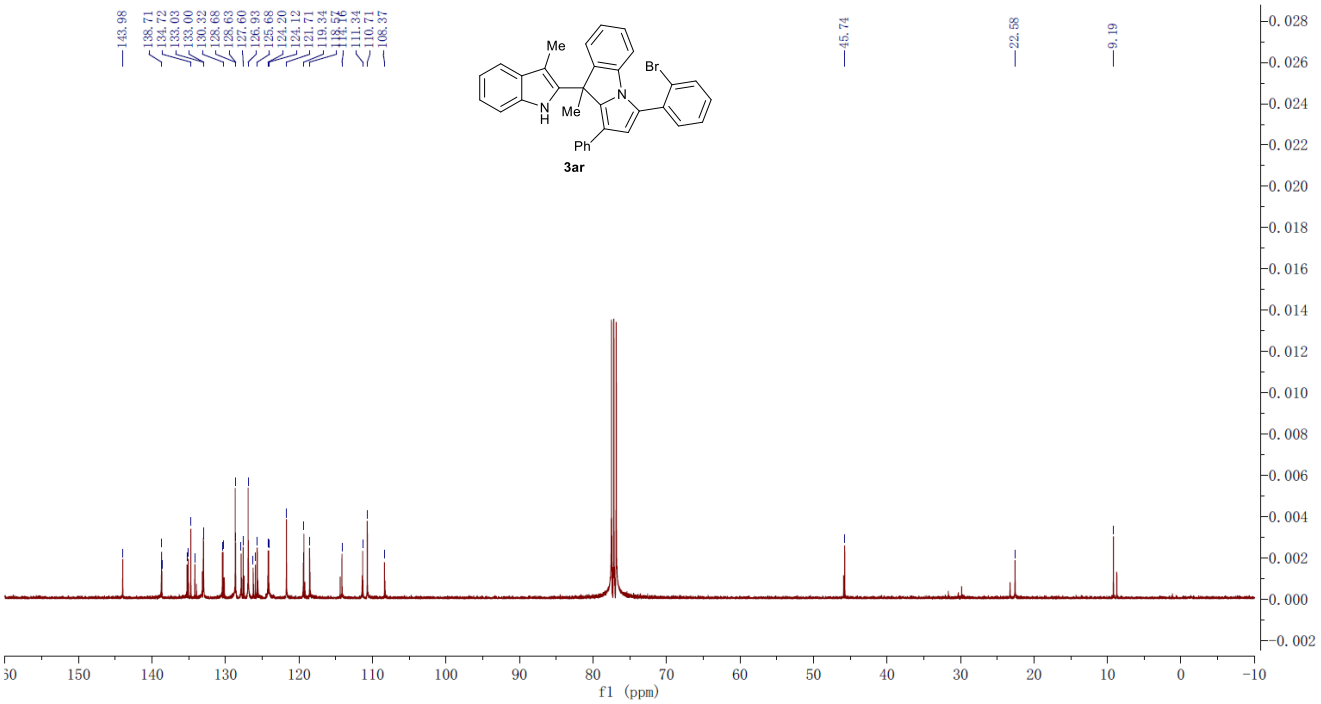
7.783
7.780
7.200
7.183
7.178
7.169
7.166
7.160
7.069
7.066
6.992
6.587
6.568
2.132
2.060
Me
Br
N
H
Me
Ph
3ar
1.45
0.85
1.02
2.14
7.02
1.01
0.98
1.24
0.96
1.01
2.99
3.00
f1 (ppm)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128.68
128.63
127.60
126.93
125.68
124.20
124.12
121.71
119.34
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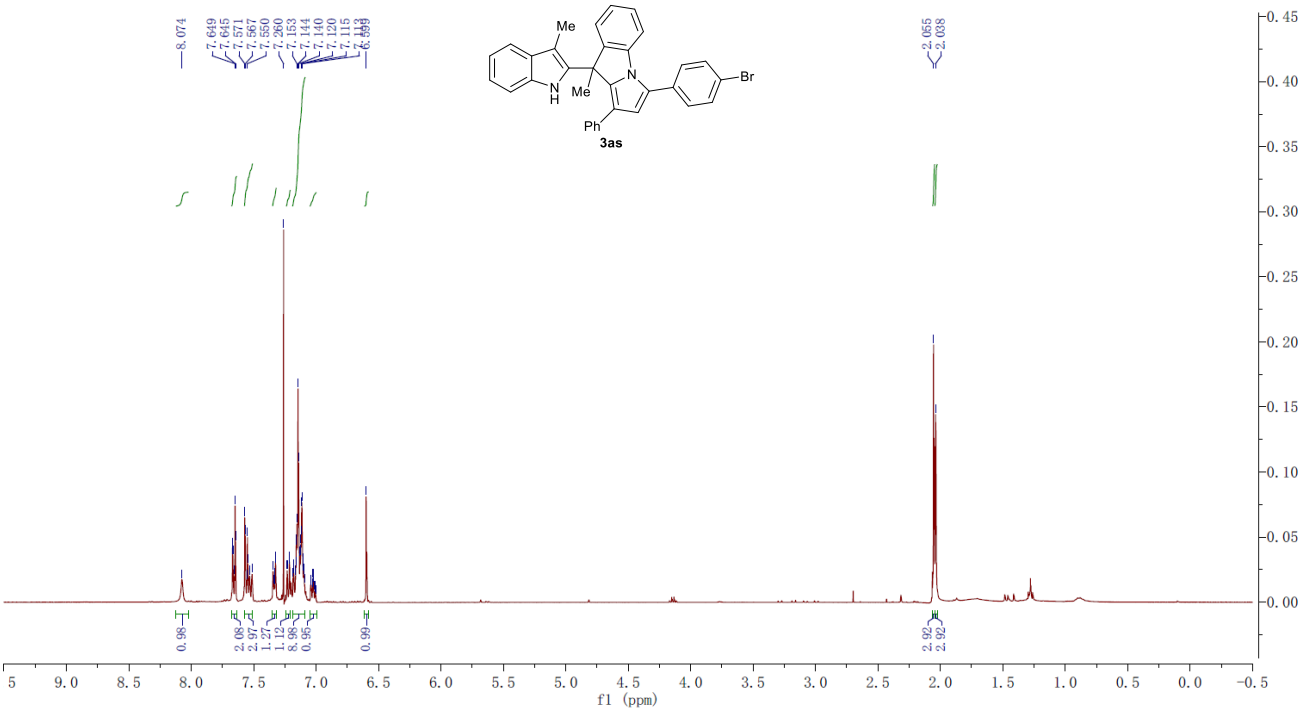
110.71
108.37
45.74
22.58
9.19
Me
Br
N
H
Me
Ph
3ar
f1 (ppm)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7.645
7.571
7.567
7.550
7.260
7.153
7.144
7.140
7.120
7.115
6.599
2.055
2.038
Me
Me
Ph
Br
N
H
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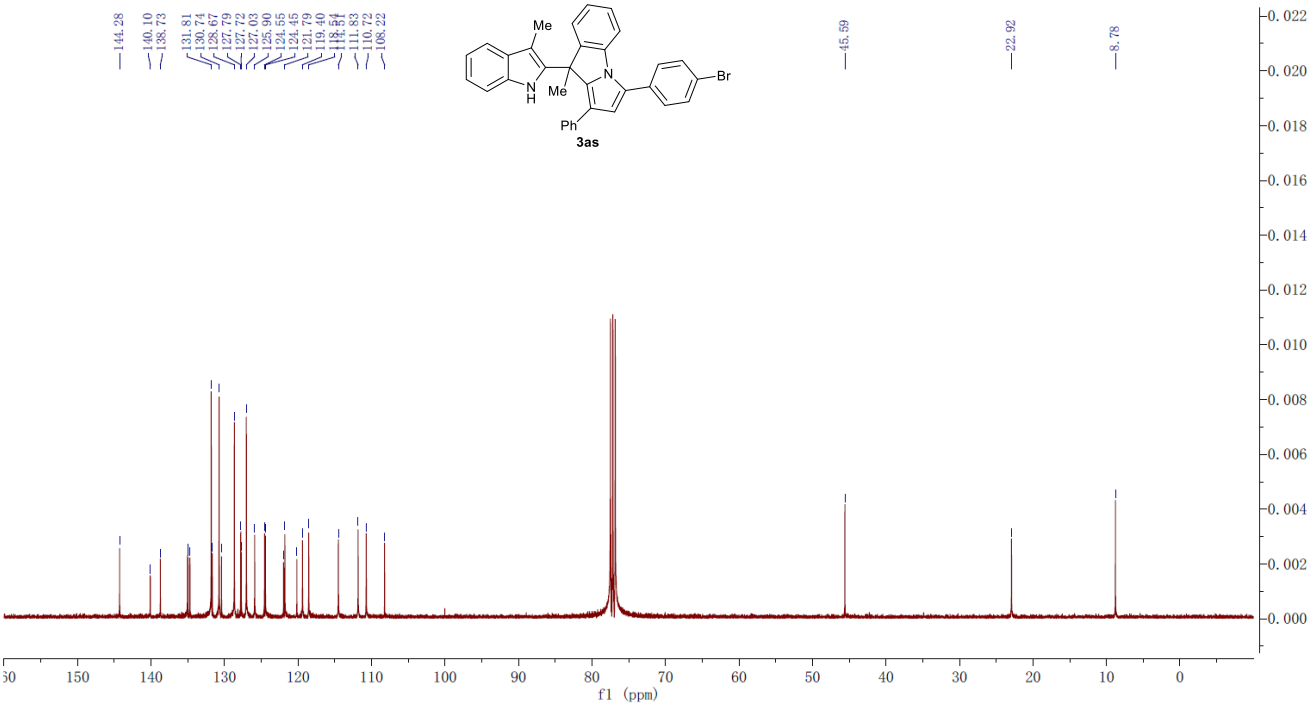
0.98
2.08
2.97
1.27
1.12
8.98
0.95
0.99
2.92
2.92
f1 (ppm)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128.67
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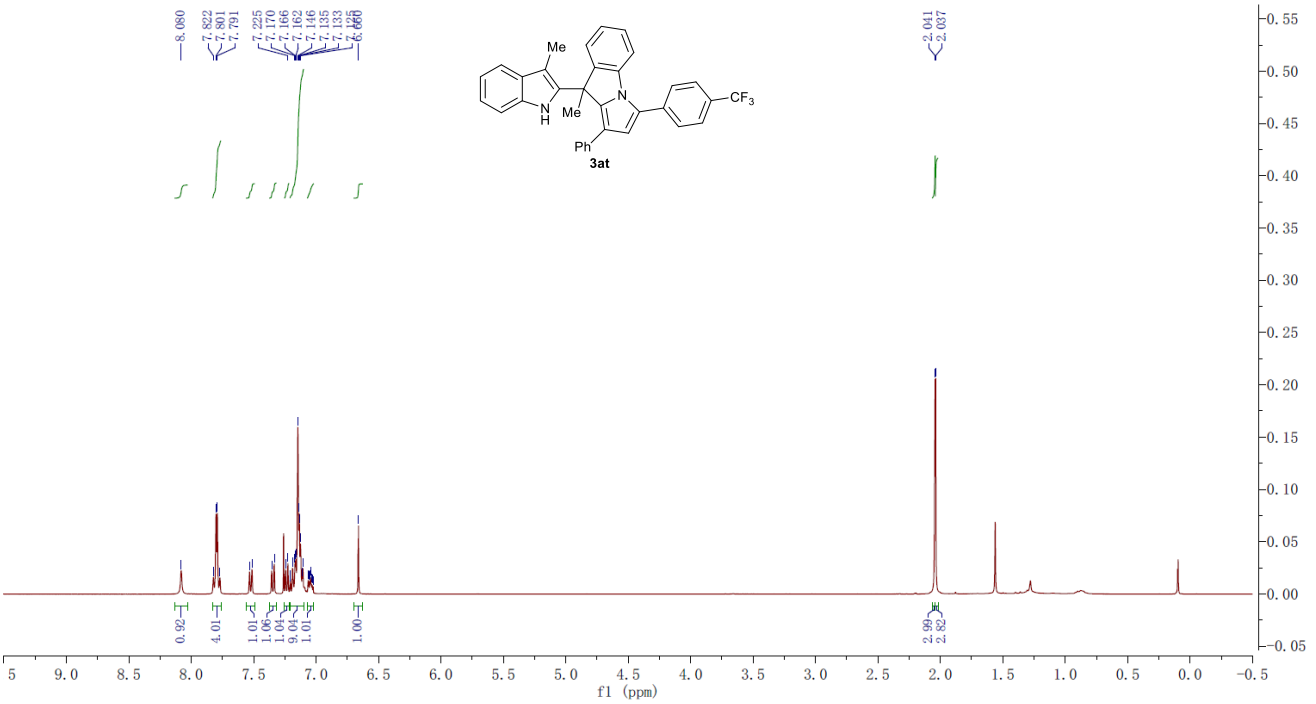
127.72
127.03
125.90
124.55
124.45
121.79
119.40
111.83
110.72
108.22
45.59
22.92
8.78
Me
Me
Ph
Br
N
H
3as
f1 (ppm)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7.170
7.166
7.162
7.146
7.135
7.133
2.041
2.037
Me
Me
N
H
N
Ph
CF3
3at
0.92
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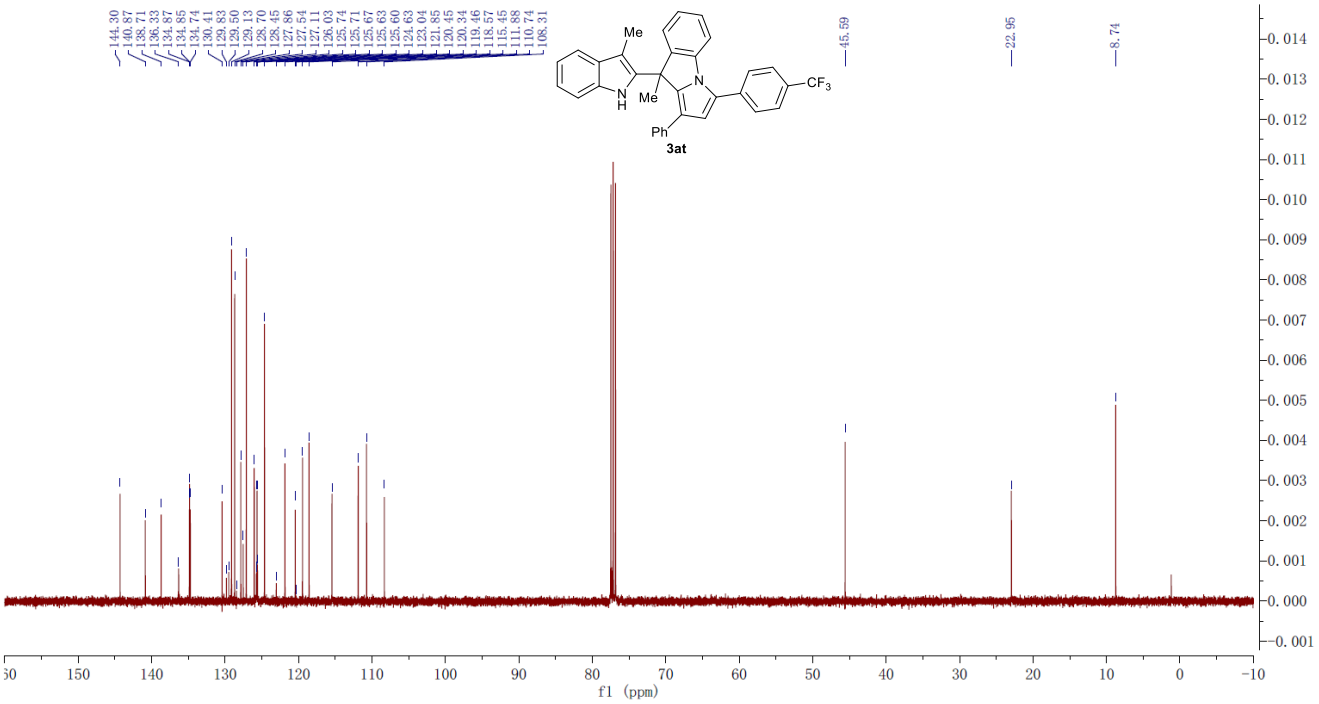
1.01
1.06
1.04
9.04
1.01
1.00
2.99
2.82
f1 (ppm)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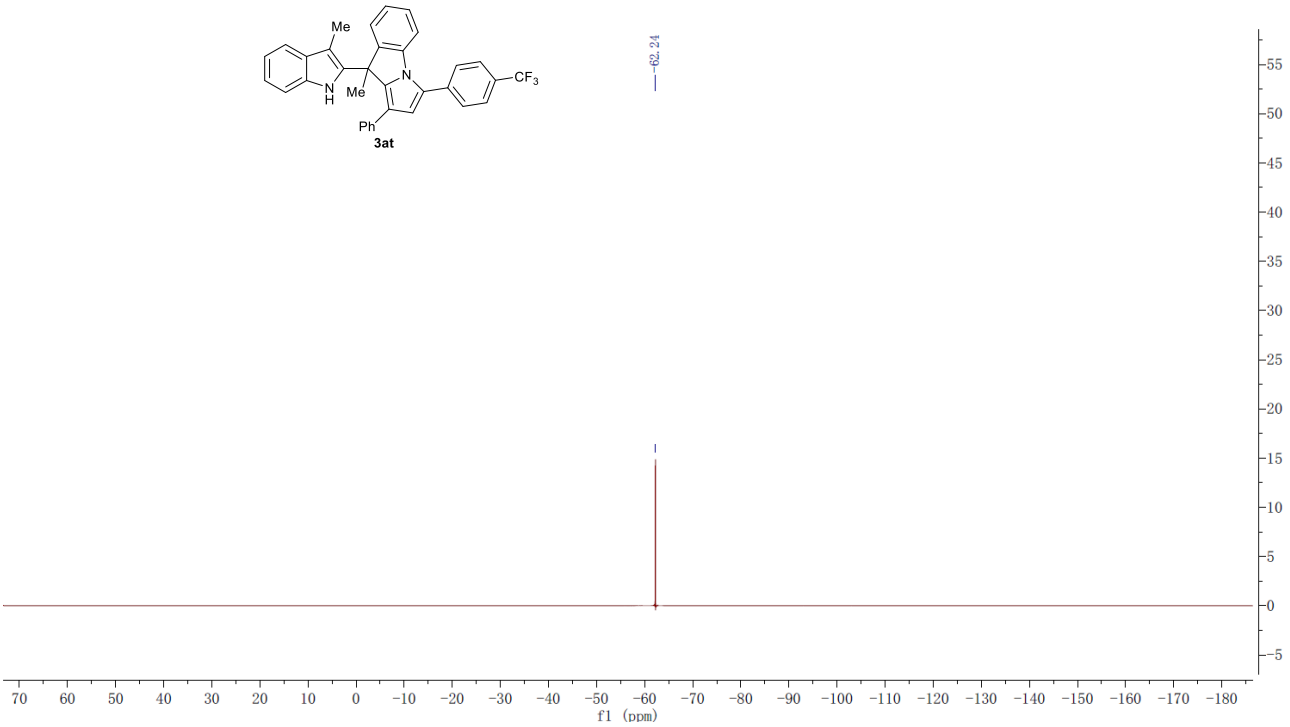
129.50
129.13
128.70
128.45
127.86
127.64
127.11
126.03
125.74
125.71
125.67
125.63
125.60
124.63
123.04
121.85
120.45
120.34
119.46
118.57
115.45
111.88
110.74
108.31
45.59
22.95
8.74
Me
Me
N
H
N
Ph
CF3
3at
f1 (ppm)


Me
Me
Ph
N
H
N
CF3
3at
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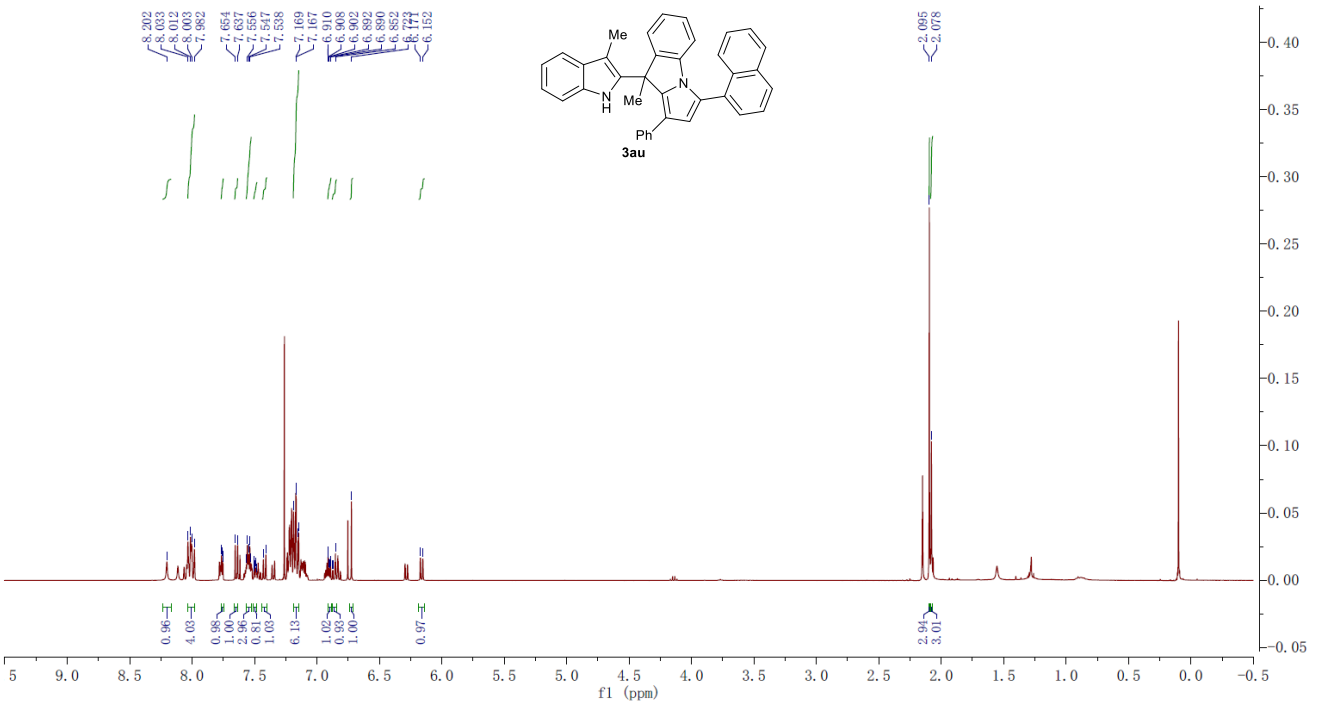
55
50
45
40
35
30
25
20
15
10
5
0
-5
70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)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8.012
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7.637
7.556
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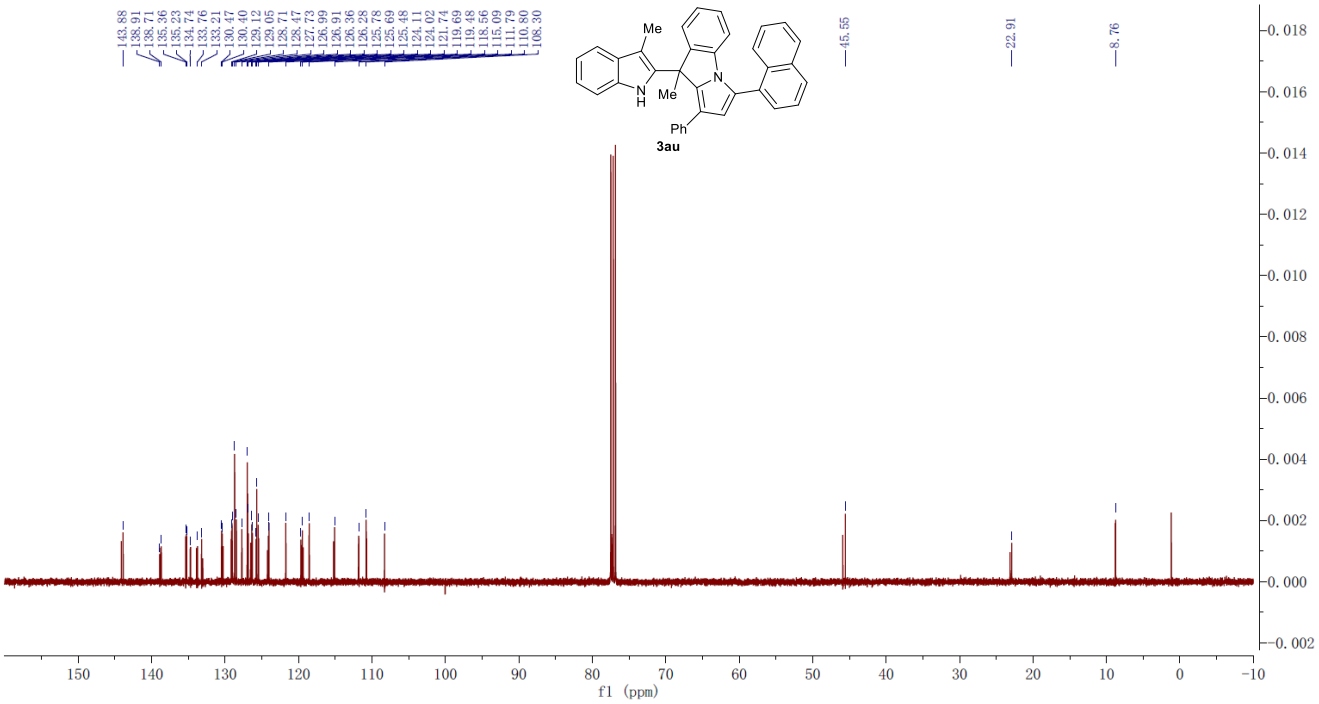
7.538
7.169
7.167
6.910
6.908
6.902
6.892
6.890
6.852
6.723
6.721
6.152
2.095
2.078
Me
Me
Ph
N
H
3au
0.96
4.03
0.98
1.00
2.96
0.81
1.03
6.13
1.02
0.93
1.00
0.97
2.94
3.01
f1 (ppm)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134.74
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130.40
129.12
129.05
128.71
128.47
127.73
126.99
126.91
126.36
126.28
125.78
125.69
125.48
124.11
124.02
121.74
121.69
119.48
118.55
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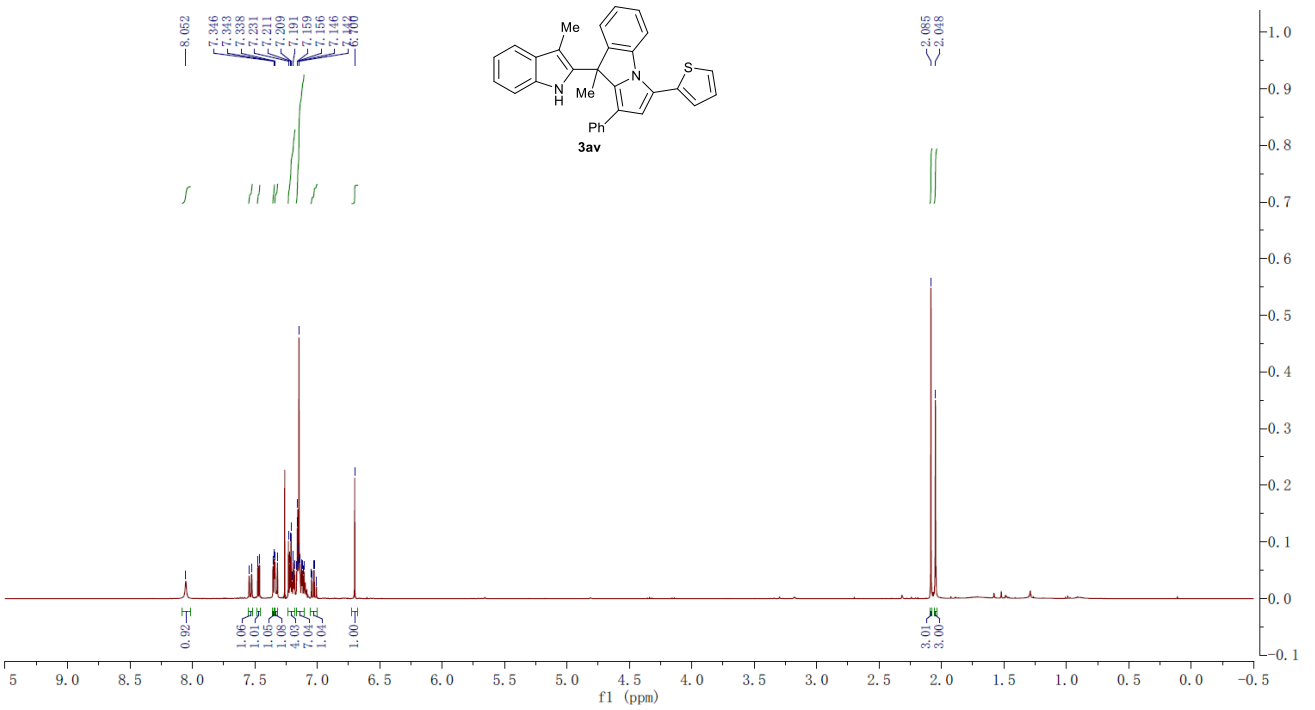
108.30
45.55
22.91
8.76
Me
Me
Ph
N
H
3au
f1 (ppm)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7.209
7.191
7.159
7.156
7.146
2.085
2.048
Me
Me
Ph
3av
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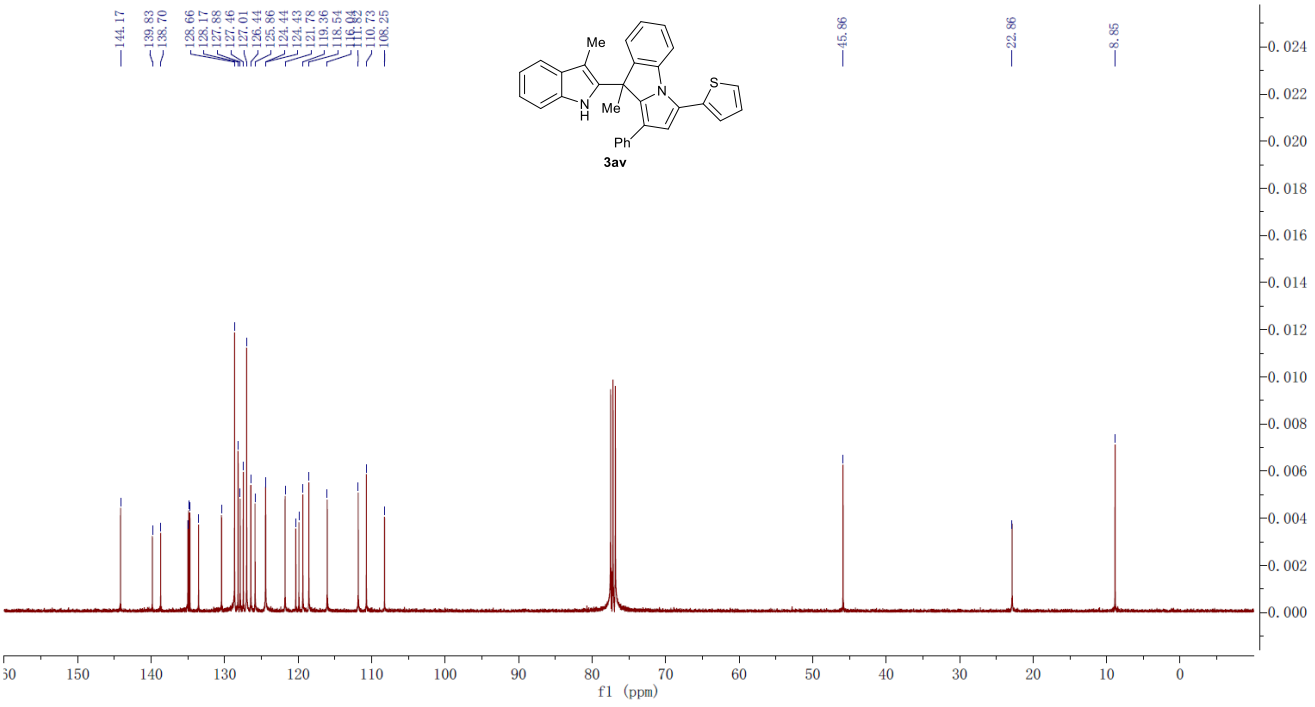
1.06
1.01
1.05
1.08
4.03
7.04
1.04
1.00
3.01
3.00
f1 (ppm)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128.17
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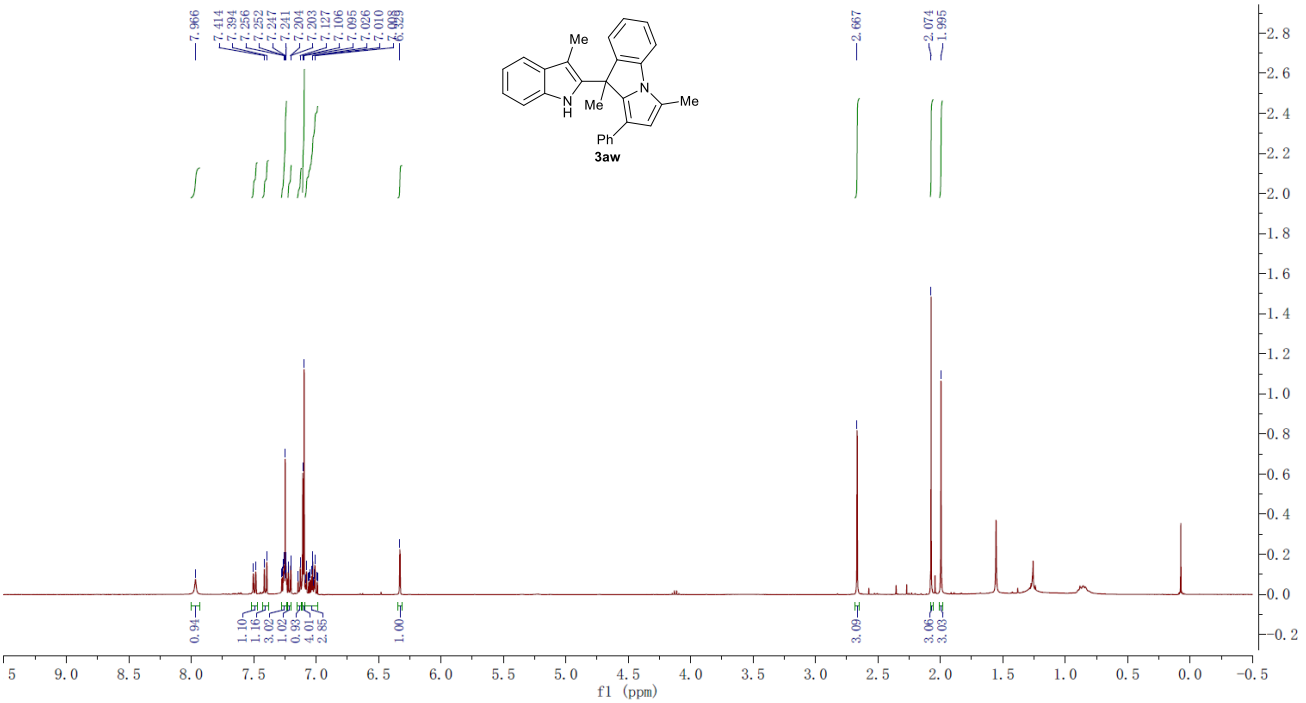
127.01
126.44
125.86
124.44
124.43
121.78
119.36
118.54
110.73
108.25
45.86
22.86
8.85
Me
Me
Ph
3av
f1 (ppm)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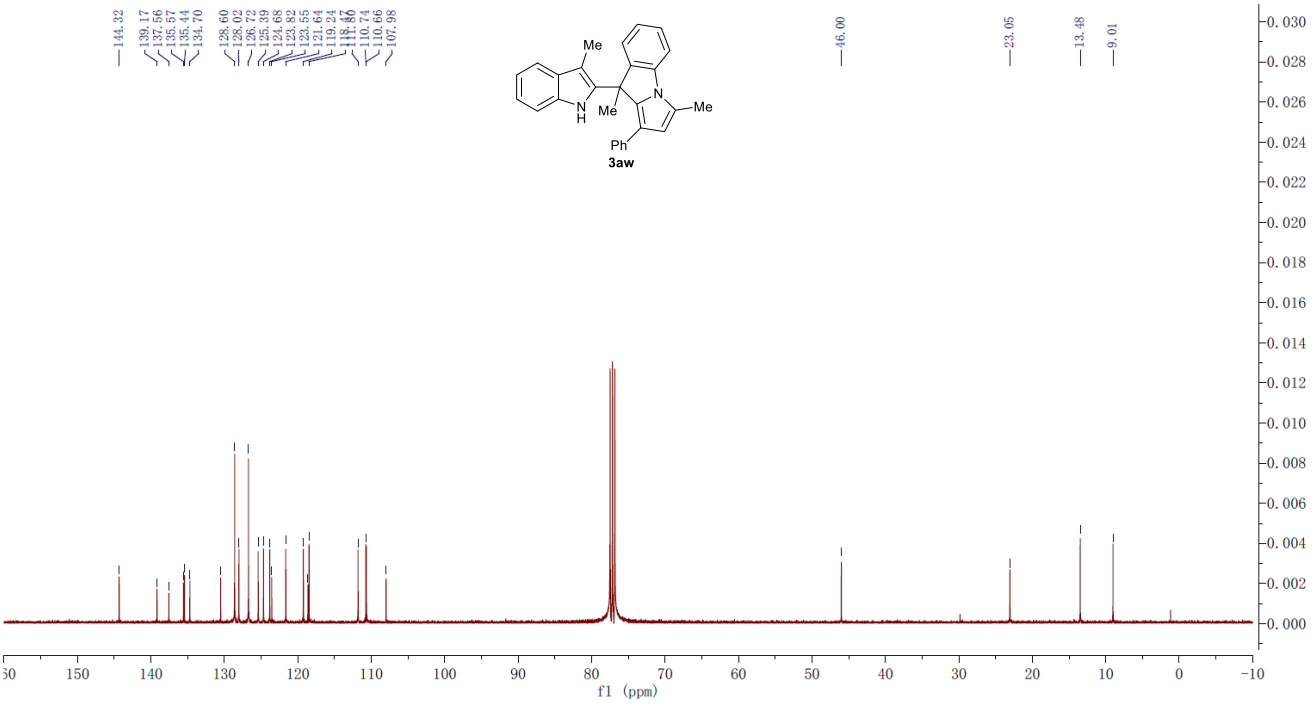
7.247
7.241
7.204
7.203
7.127
7.106
7.095
7.026
7.010
6.329
2.667
2.074
1.995
Me
Me
Me
Ph
3aw
0.94
1.10
1.16
3.02
1.02
0.93
4.01
2.85
1.00
3.09
3.06
3.03
f1 (ppm)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128.02
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125.39
124.68
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123.55
121.64
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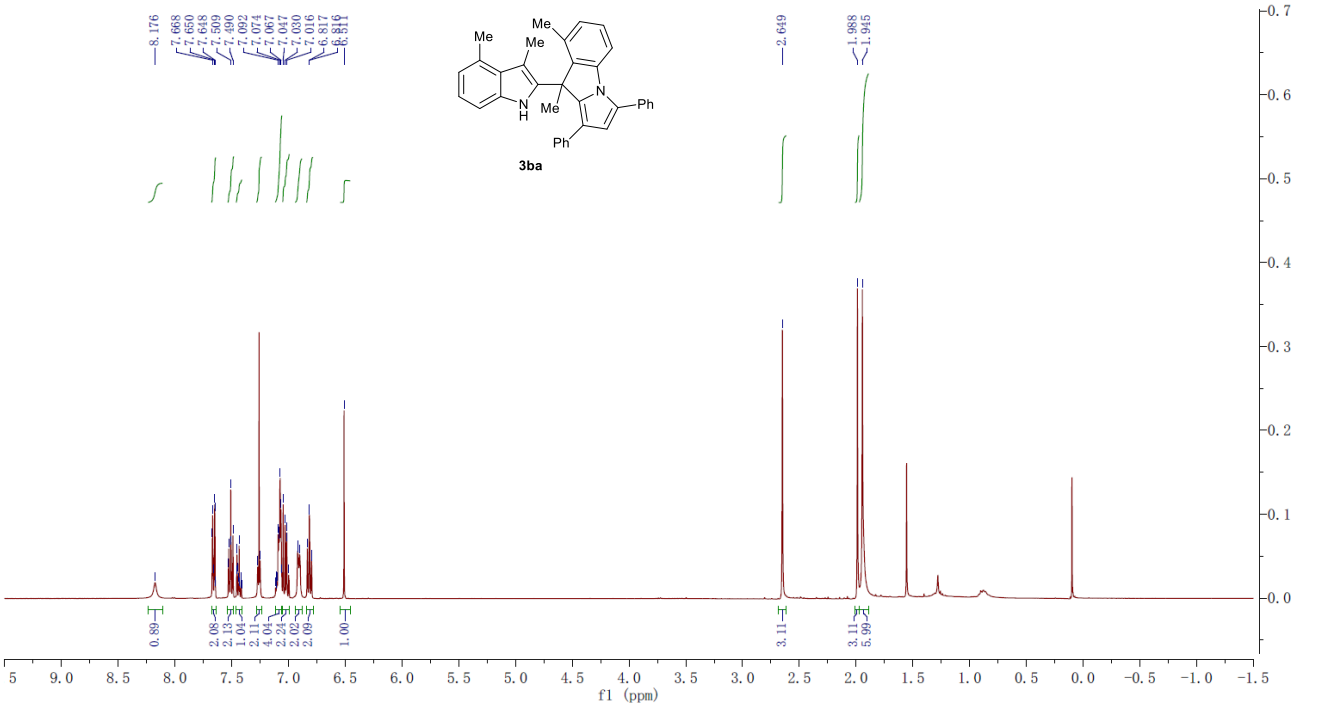
46.00
23.05
13.48
9.01
Me
Me
Me
Ph
3aw
f1 (ppm)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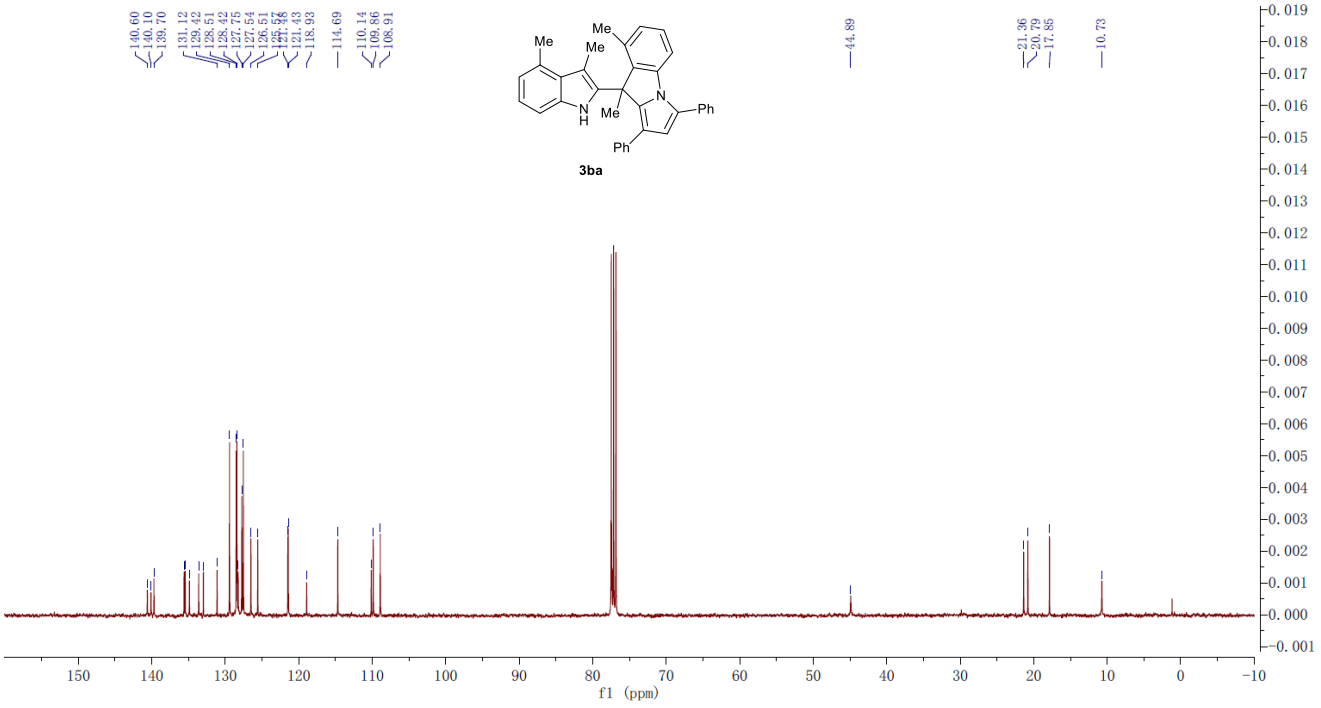
7.067
7.047
7.030
7.016
6.817
6.811
2.649
1.988
1.945
Me
Me
Me
N
H
Me
N
Ph
Ph
3ba
0.89
2.08
2.13
1.04
2.11
4.04
2.24
2.02
2.09
1.00
3.11
3.11
5.99
f1 (ppm)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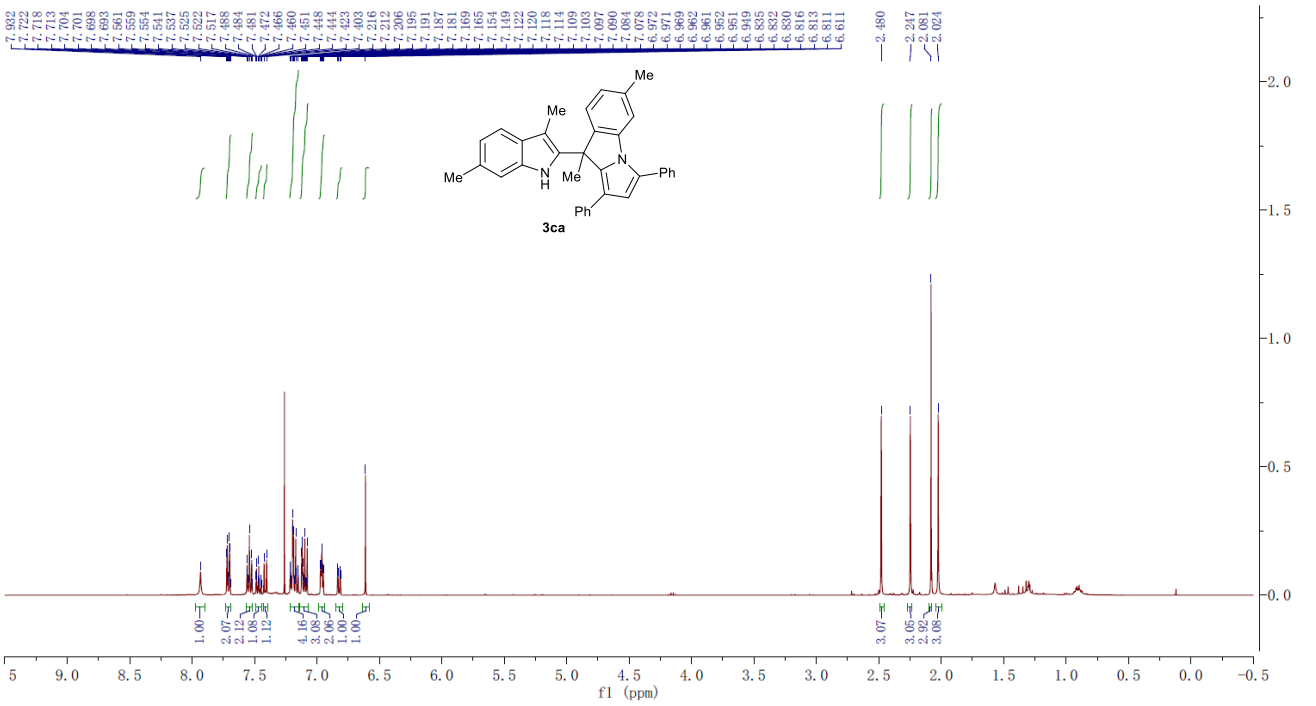
126.51
121.43
118.93
114.69
110.14
109.86
108.91
44.89
21.36
20.79
17.85
10.73
Me
Me
Me
N
H
Me
N
Ph
Ph
3ba
f1 (ppm)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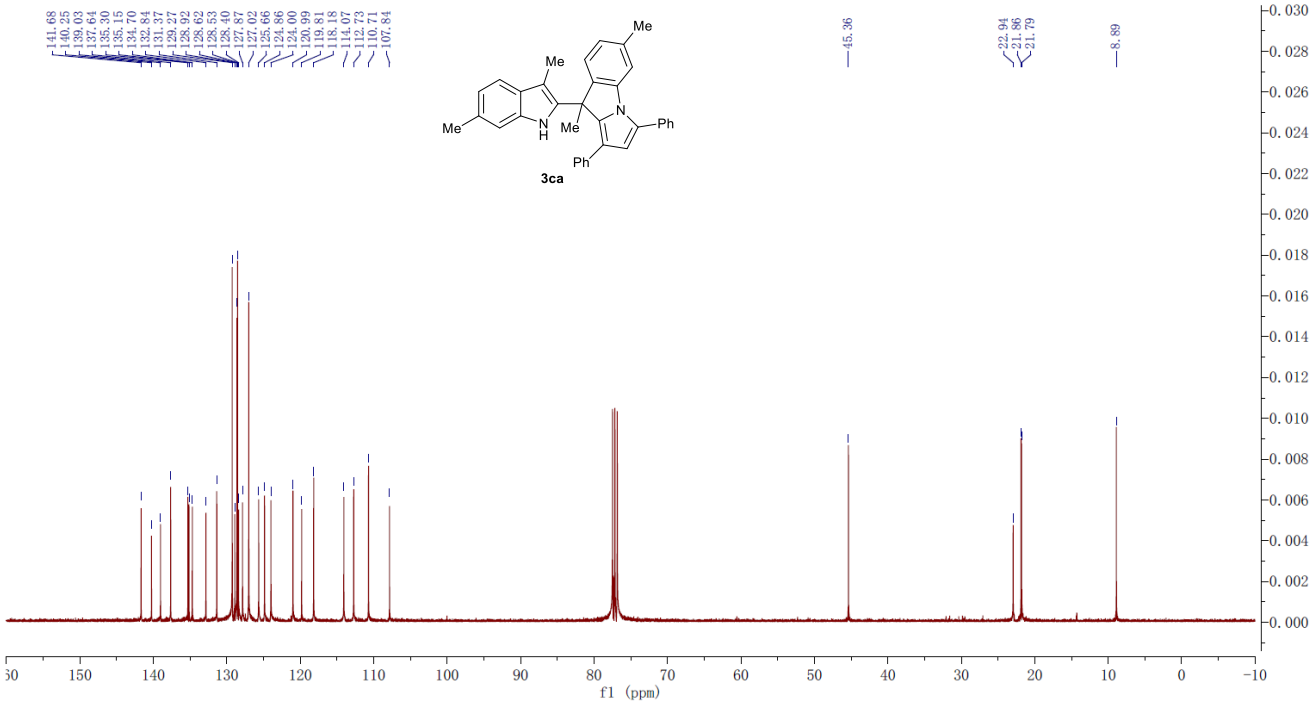
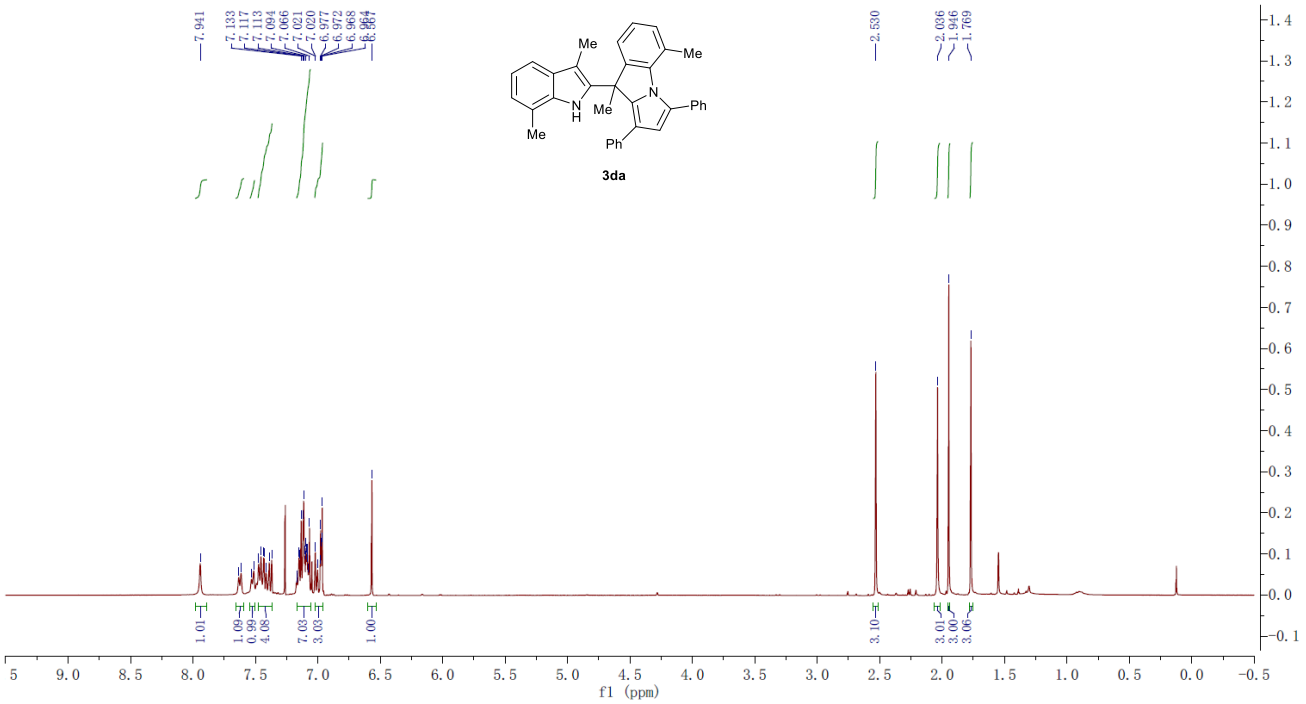
Me
Me
N
H
Me
N
Ph
Ph
3ca
f1 (ppm)


Me
Me
Me
N
H
Me
N
Ph
Ph
3ca
f1 (ppm)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7.021
7.020
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6.972
6.968
2.530
2.036
1.946
1.769
Me
Me
Me
N
H
Me
Ph
Ph
3da
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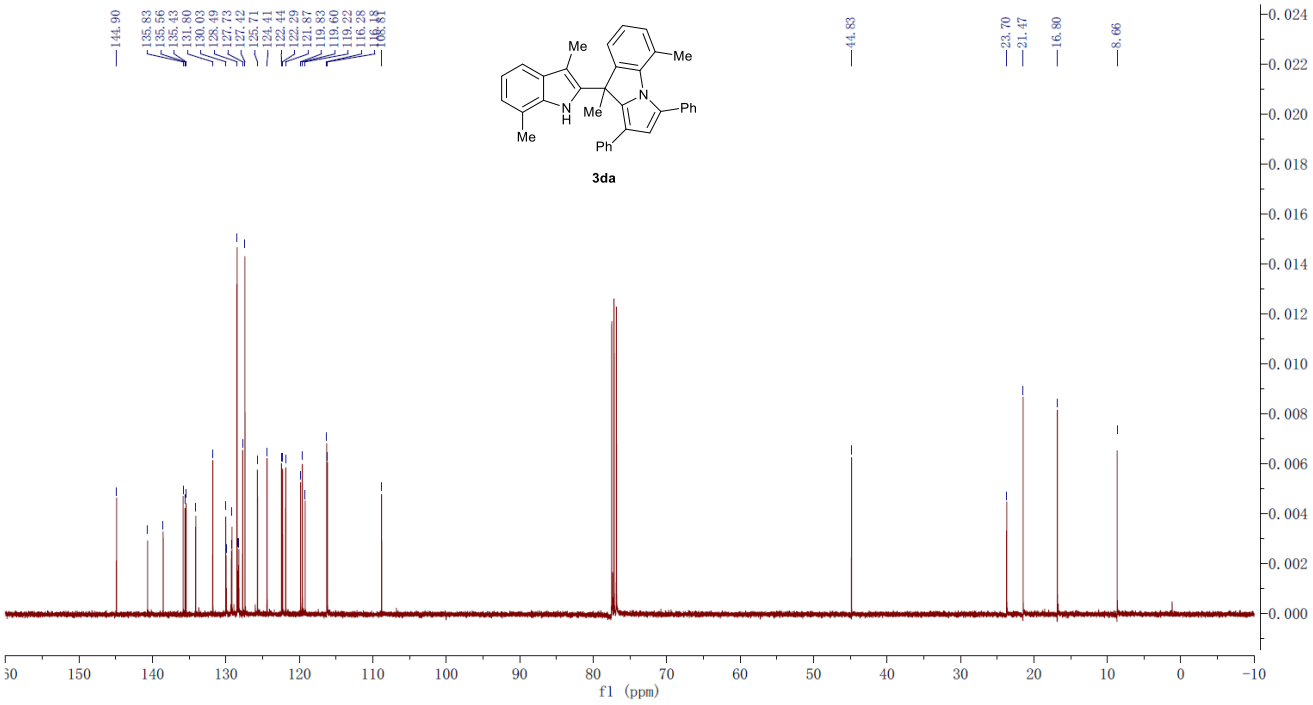
4.08
7.03
3.03
1.00
3.10
3.01
3.00
3.06
f1 (ppm)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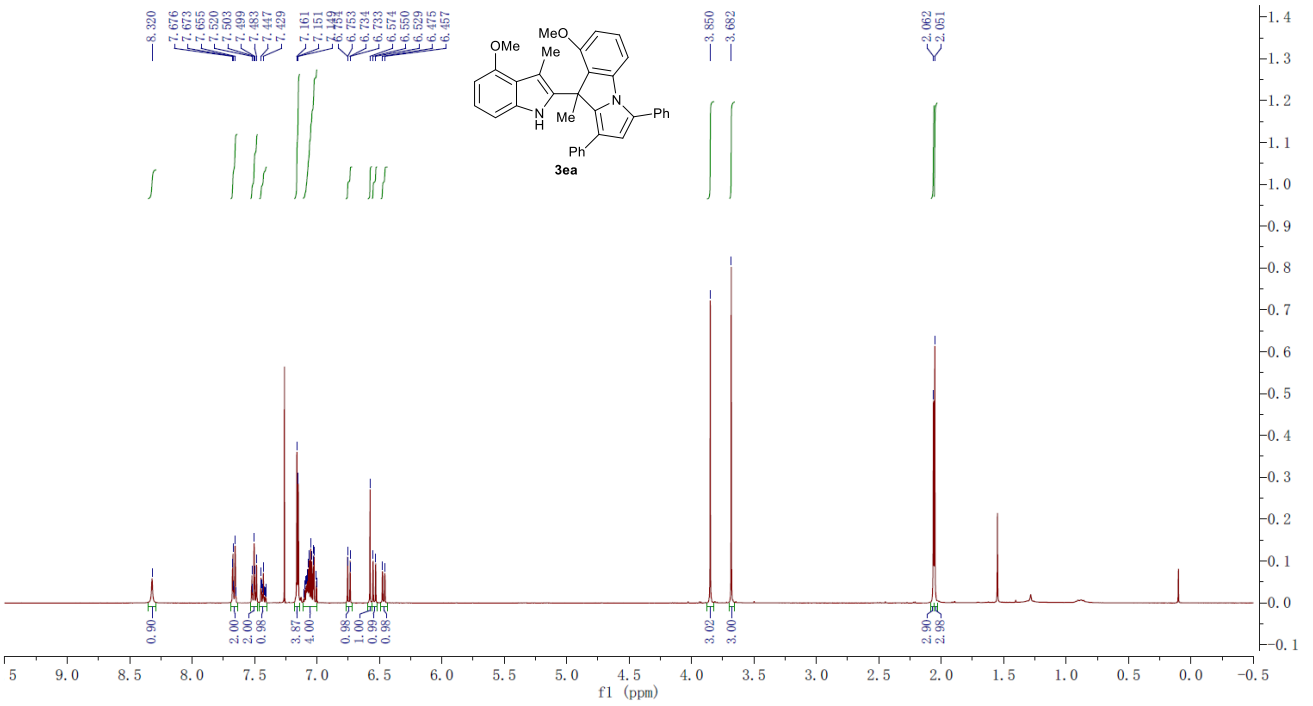
122.29
121.87
119.83
119.60
119.22
116.28
44.83
23.70
21.47
16.80
8.66
Me
Me
Me
N
H
Me
Ph
Ph
3da
f1 (ppm)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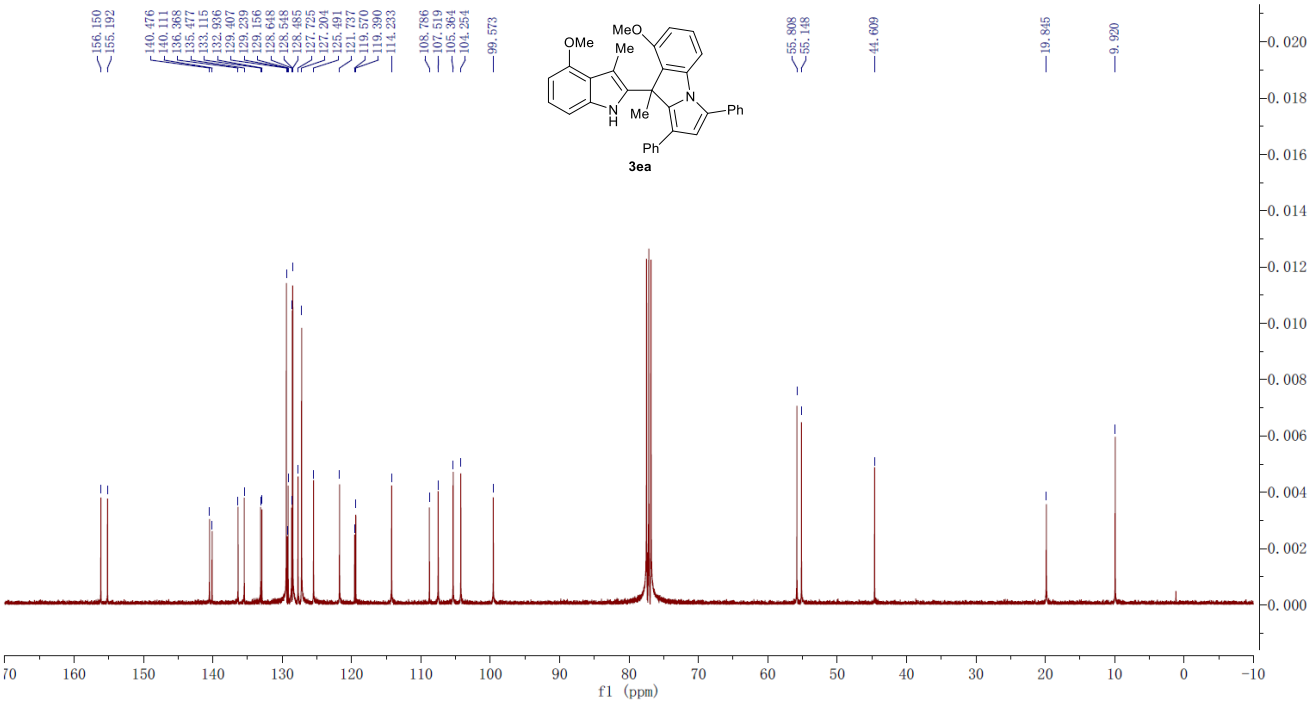
7.676
7.673
7.655
7.520
7.503
7.499
7.483
7.447
7.429
7.161
7.151
6.753
6.734
6.733
6.574
6.550
6.529
6.475
6.457
3.850
3.682
2.062
2.051
OMe
MeO
Me
N
H
Me
N
Ph
Ph
3ea
0.90
2.00
2.00
0.98
3.87
4.00
0.98
1.00
0.99
0.98
3.02
3.00
2.90
2.98
f1 (ppm)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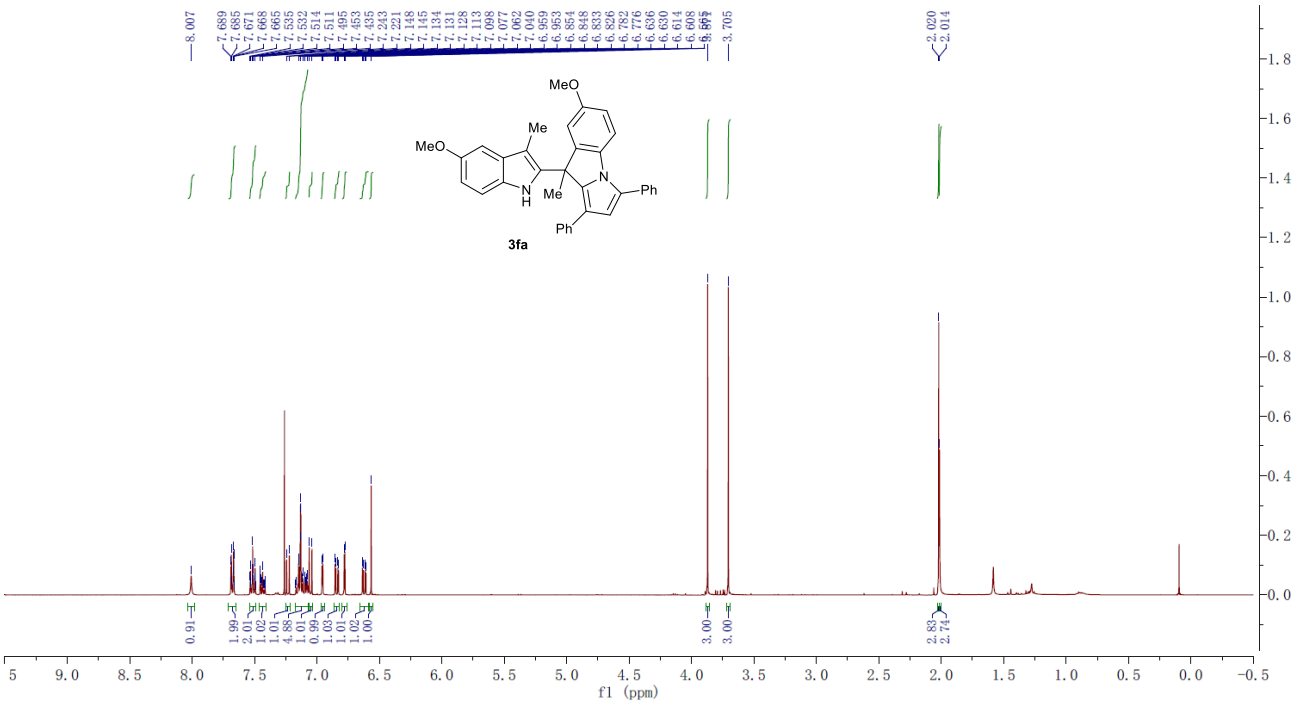
155.192
140.476
140.111
136.368
136.177
133.115
132.936
129.407
129.239
129.156
128.648
128.548
128.485
127.725
127.204
125.491
121.737
119.570
119.390
114.233
108.786
107.519
105.364
104.254
99.573
55.808
55.148
44.609
19.845
9.920
OMe
MeO
Me
N
H
Me
N
Ph
Ph
3ea
f1 (ppm)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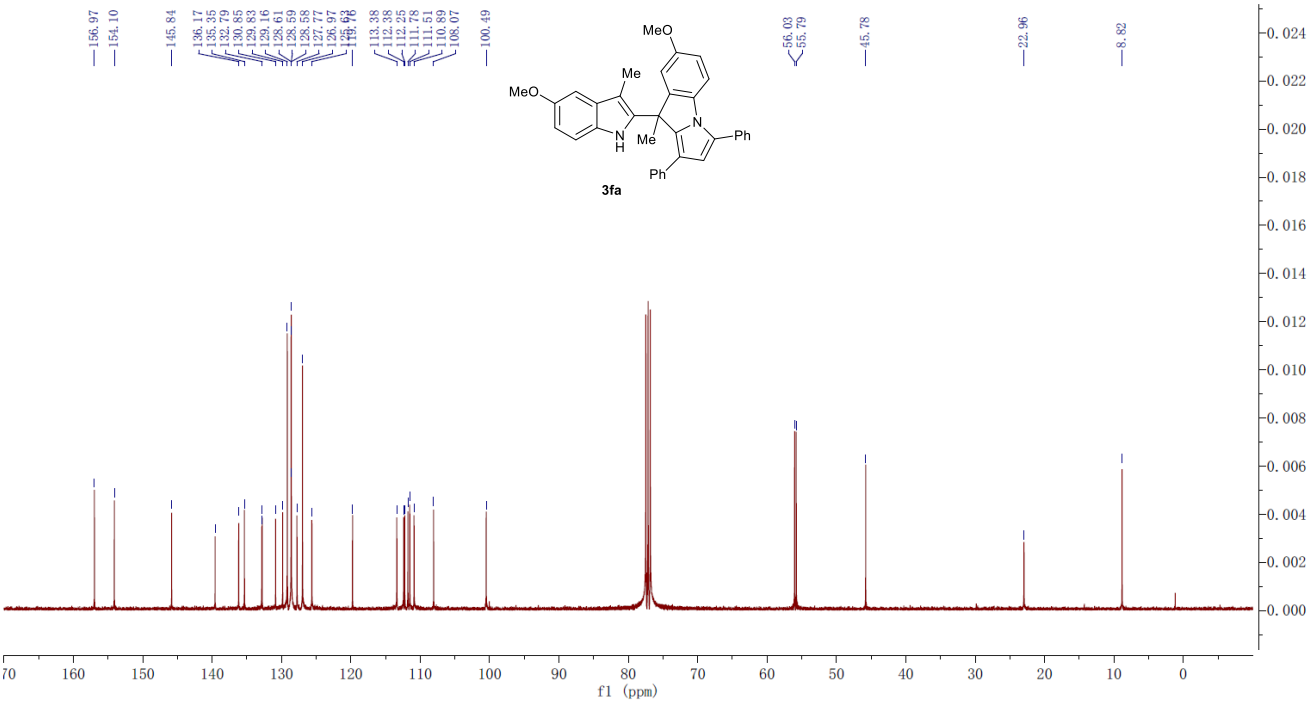
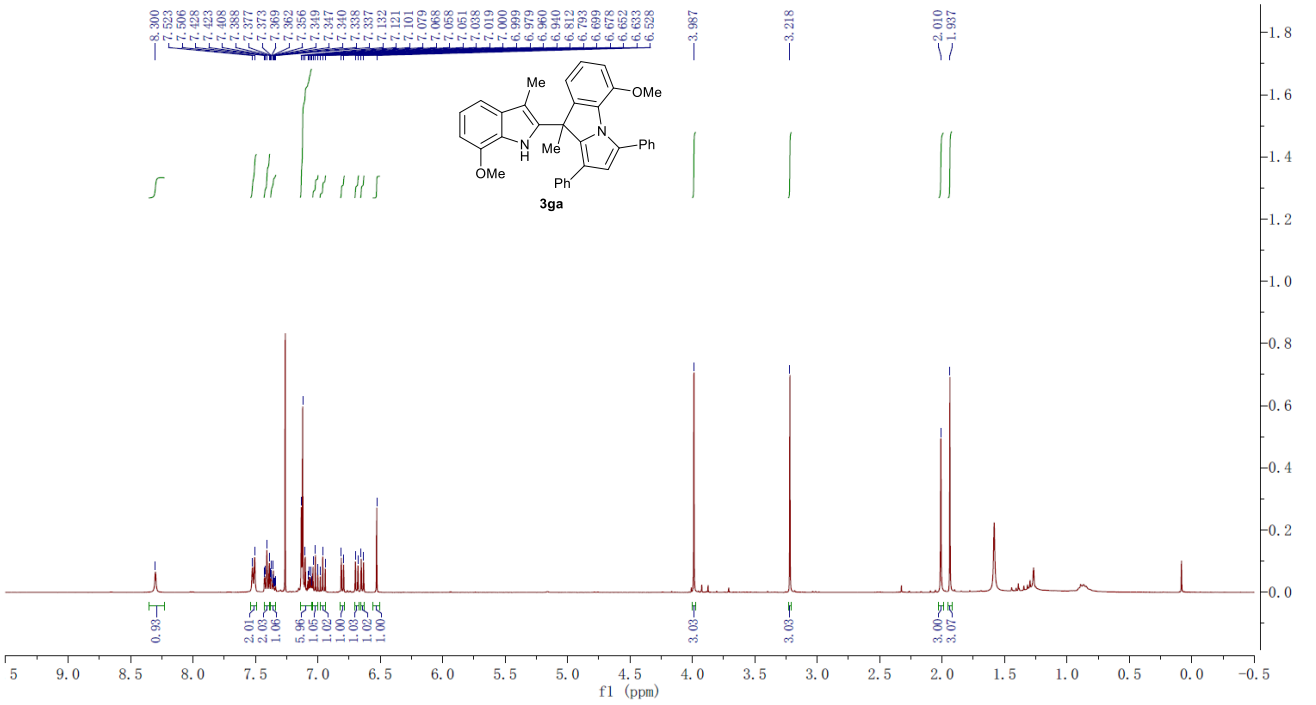
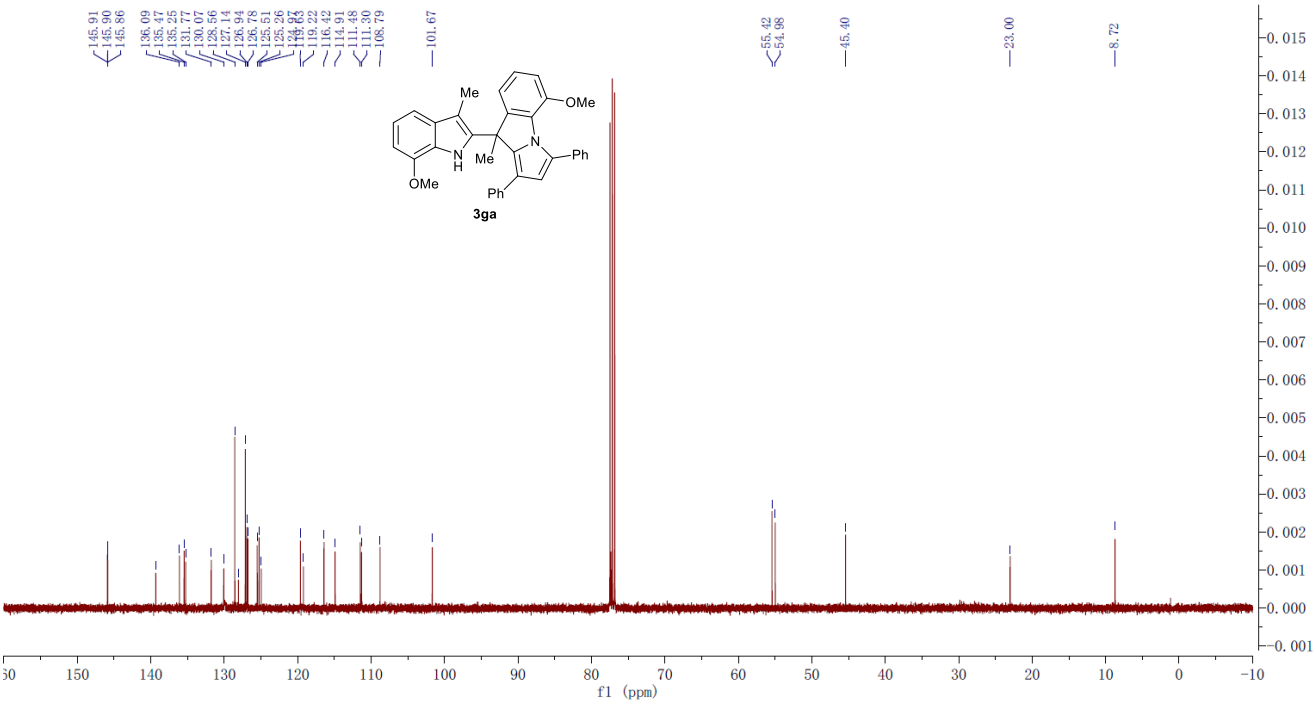
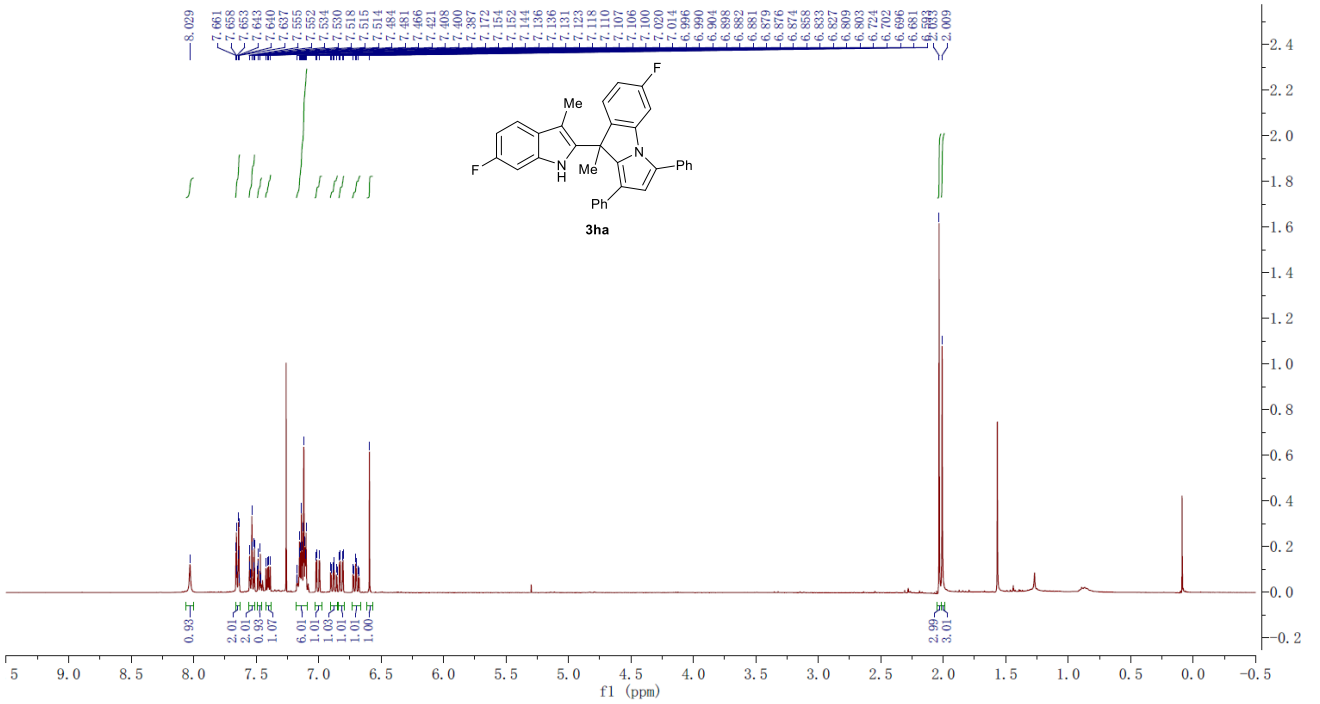
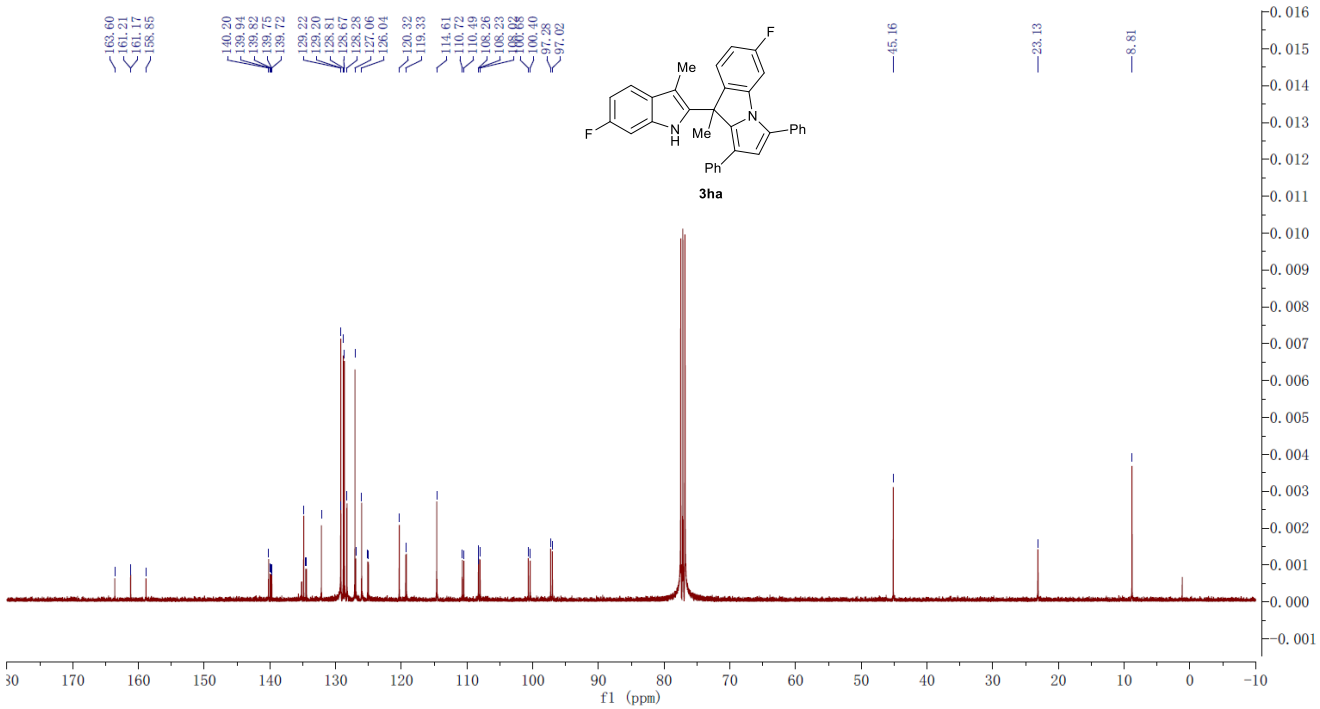
7.685
7.671
7.668
7.665
7.535
7.532
7.514
7.511
7.495
7.453
7.435
7.243
7.221
7.148
7.145
7.134
7.131
7.128
7.113
7.098
7.077
7.062
7.040
6.959
6.953
6.854
6.848
6.833
6.526
6.782
6.776
6.636
6.630
6.614
6.608
3.705
2.020
2.014
MeO
Me
MeO
N
H
Me
N
Ph
Ph
3fa
0.91
1.99
2.01
1.02
1.01
4.01
0.99
1.03
1.01
1.02
1.00
3.00
3.00
2.83
2.74
f1 (ppm)

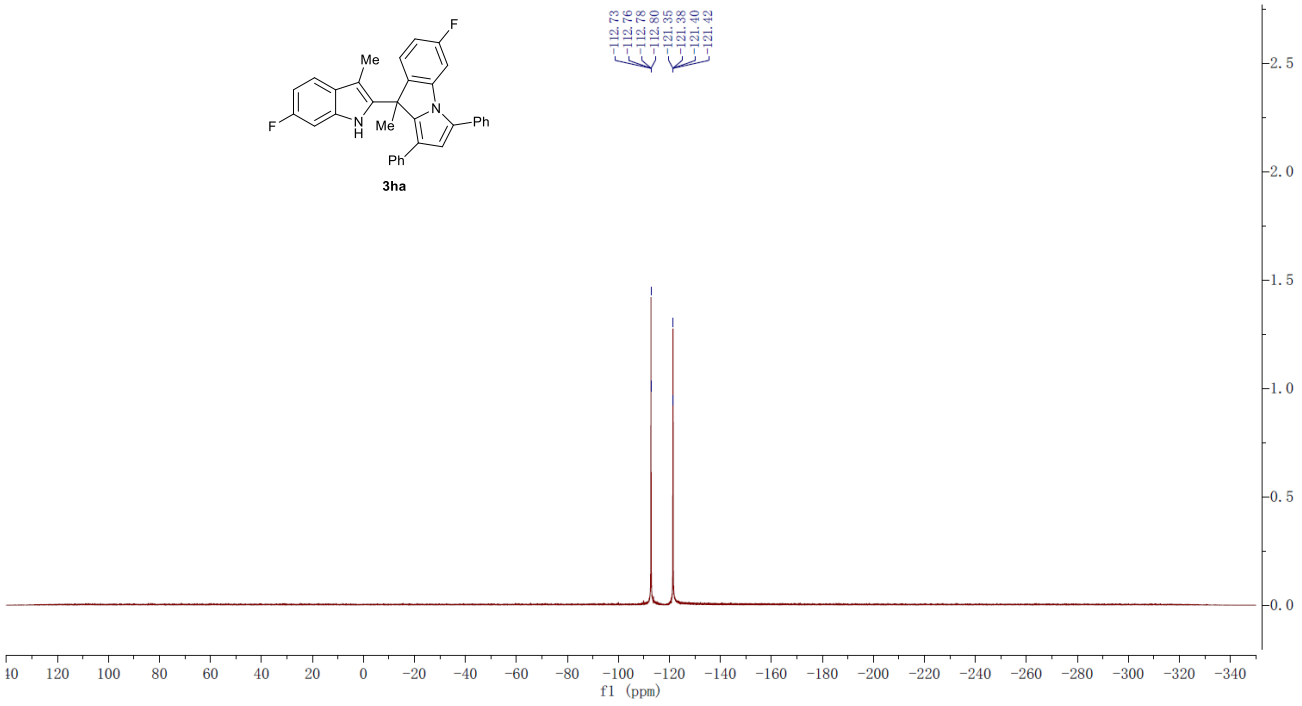

156.97
154.10
145.84
136.17
135.35
132.79
130.85
129.83
129.16
128.61
128.59
128.58
127.77
126.97
113.38
112.38
112.25
111.78
111.51
110.89
108.07
100.49
56.03
55.79
45.78
22.96
8.82
MeO
Me
MeO
N
H
Me
N
Ph
Ph
3fa
f1 (ppm)

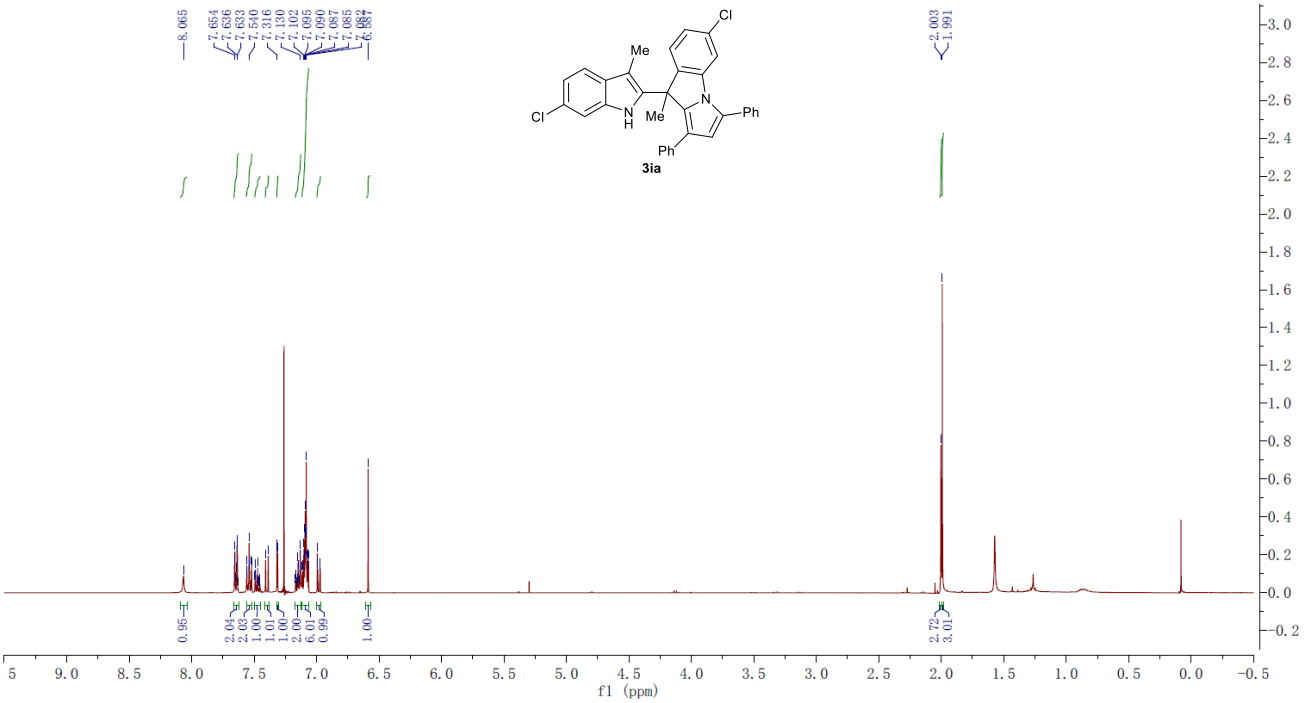

Me
OMe
N
H
Me
N
Ph
OMe
Ph
3ga
f1 (ppm)

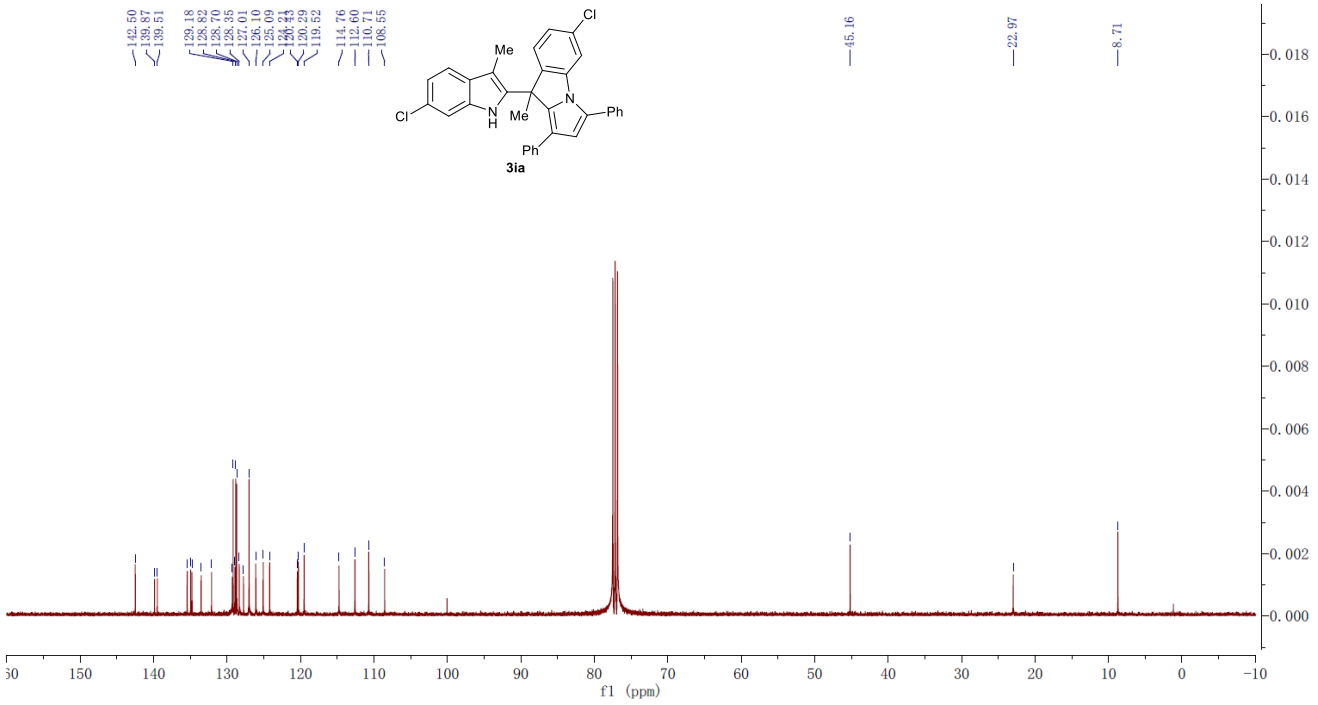

Me
OMe
N
H
Me
N
Ph
OMe
Ph
3ga
f1 (ppm)

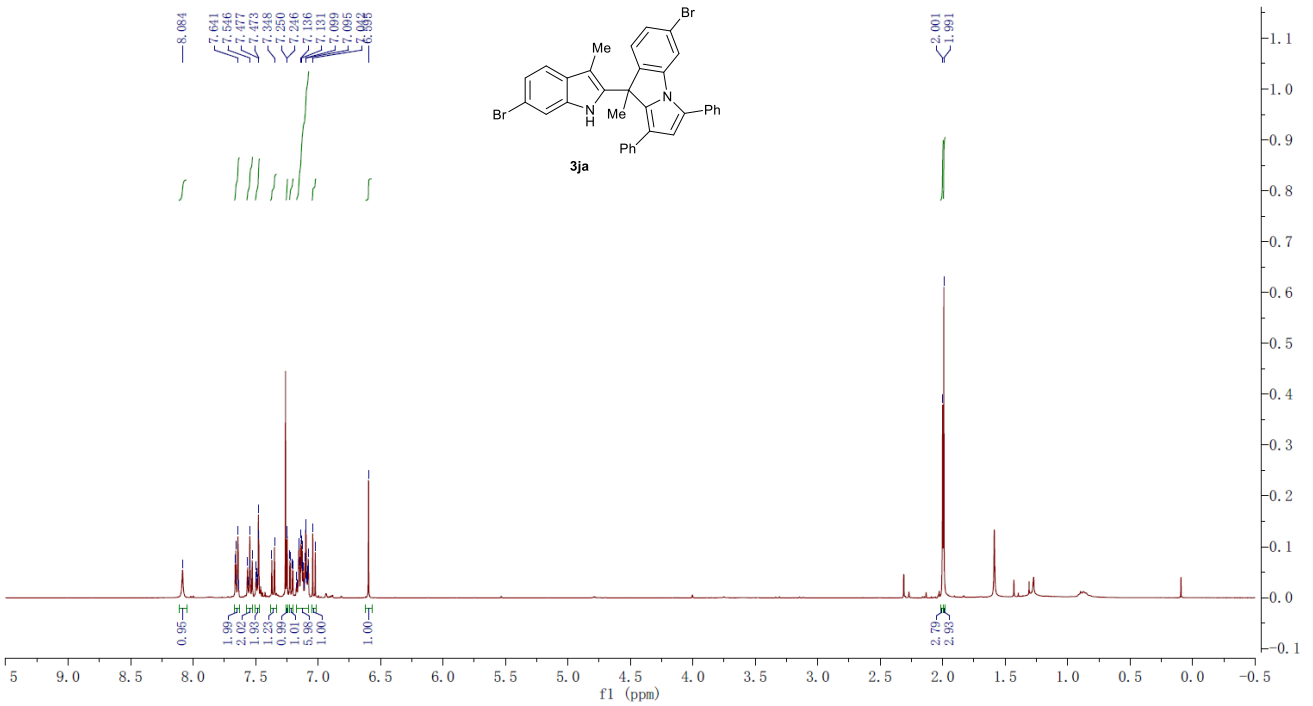

3ha
f1 (ppm)

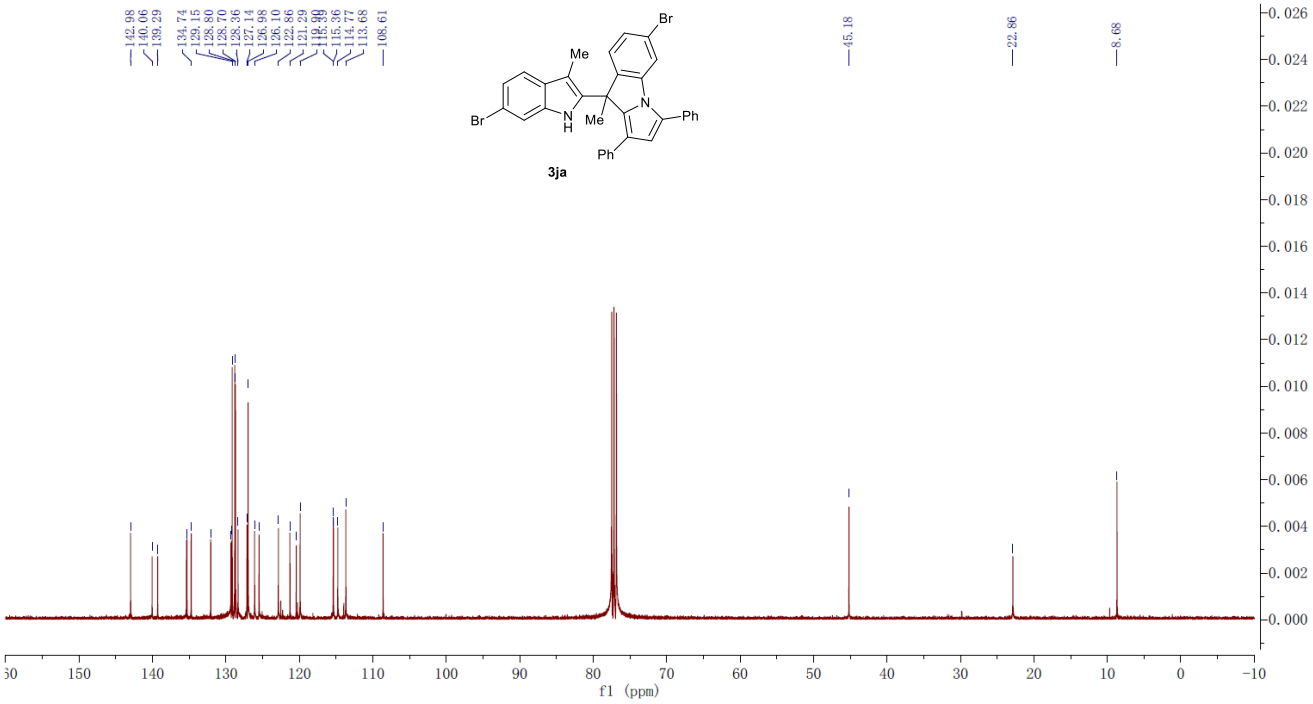

3ha
f1 (ppm)

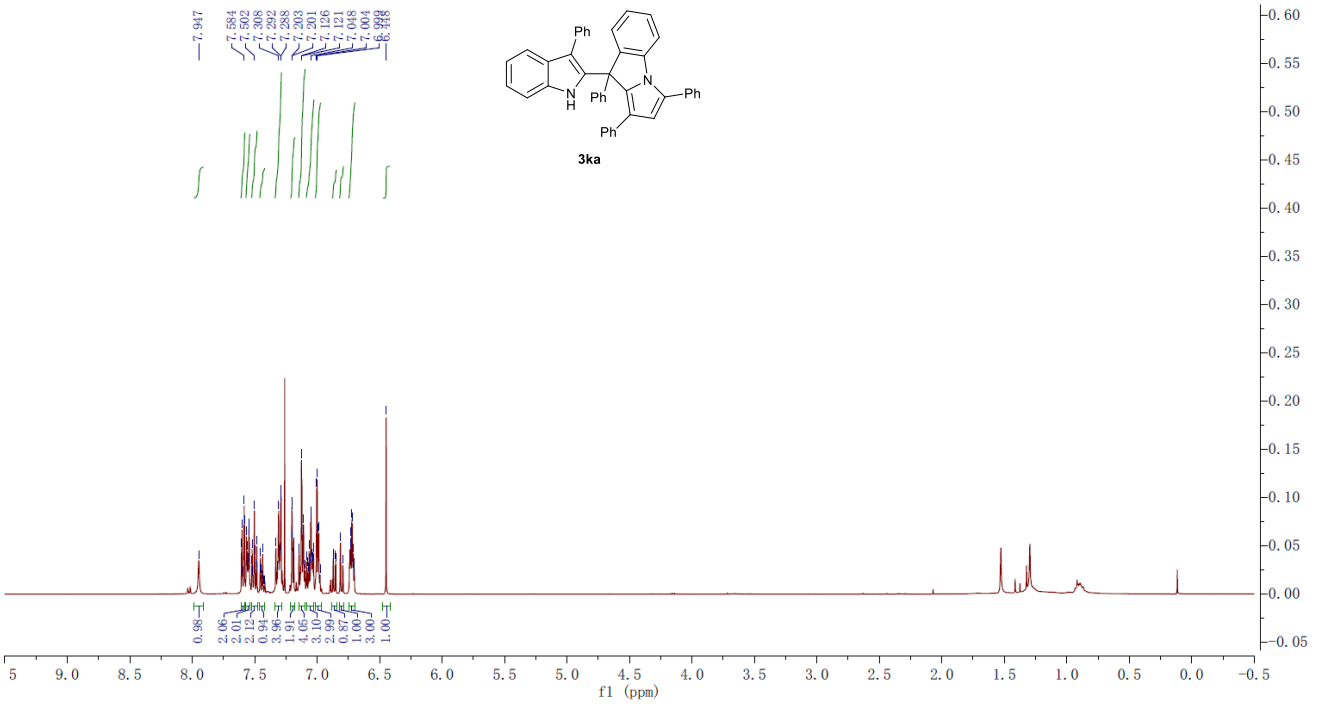

F
Me
F
N
H
Me
N
Ph
Ph
3ha
-112.73
-112.76
-112.78
-112.80
-121.35
-121.38
-121.40
-121.42
2.5
2.0
1.5
1.0
0.5
0.0
40 120 100 80 60 40 20 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240 -260 -280 -300 -320 -340
f1 (ppm)

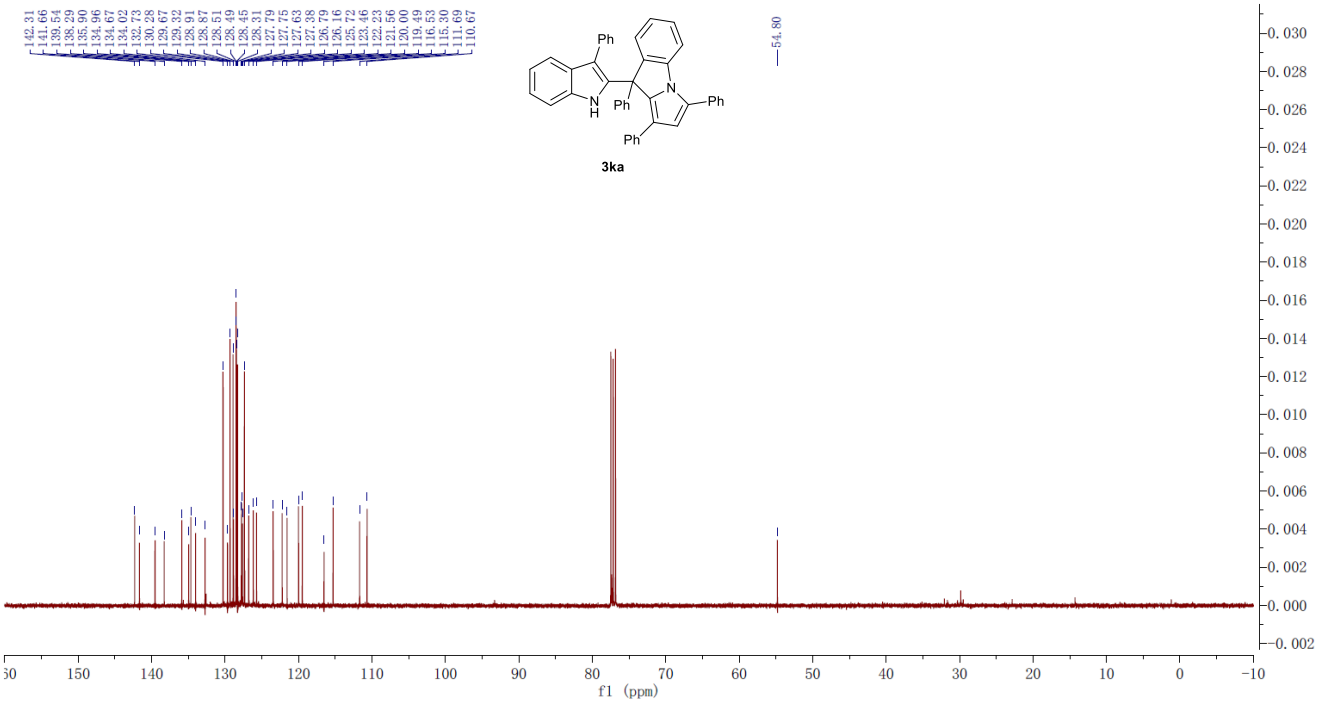

8.065
7.654
7.636
7.633
7.540
7.316
7.130
7.102
7.095
7.090
7.087
7.085
6.584
6.582
2.003
1.991
Me
Cl
N
H
Me
N
Ph
Ph
3ia
0.95
2.04
2.03
1.00
1.01
1.00
2.00
6.01
0.99
1.00
2.72
3.01
f1 (ppm)

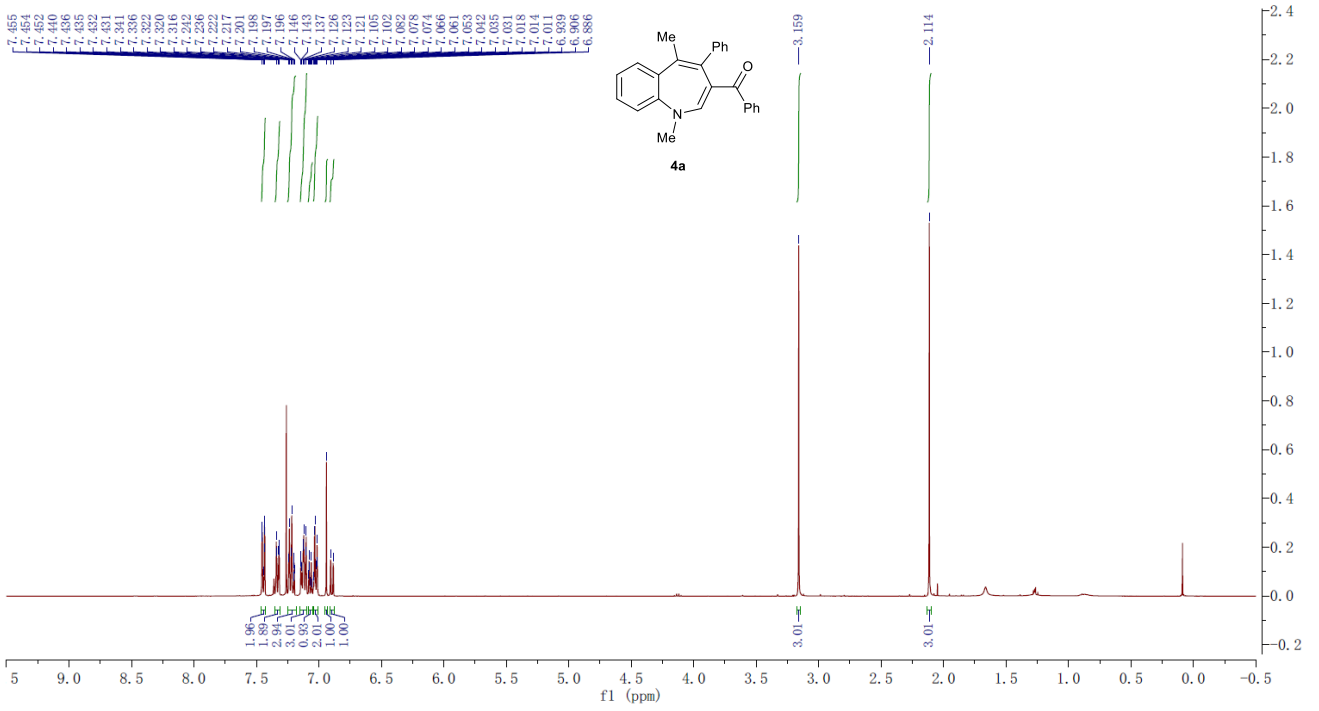

142.50
139.87
139.51
129.18
128.82
128.70
128.35
127.01
126.10
125.09
120.29
119.52
114.76
112.60
110.71
108.55
45.16
22.97
8.71
Me
Cl
N
H
Me
N
Ph
Ph
3ia
f1 (ppm)


8.084
7.641
7.546
7.477
7.473
7.348
7.250
7.246
7.136
7.131
7.099
7.095
6.935
2.001
1.991
Br
Me
N
H
Me
N
Ph
Ph
3ja
0.95
1.99
2.02
1.93
1.23
0.99
1.01
5.98
1.00
1.00
2.79
2.93
f1 (ppm)


142.98
140.06
139.29
134.74
129.15
128.80
128.70
128.36
127.14
126.98
126.10
122.86
121.29
115.36
114.77
113.68
108.61
45.18
22.86
8.68
Br
Me
N
H
Me
N
Ph
Ph
3ja
f1 (ppm)


7.947
7.584
7.582
7.308
7.292
7.288
7.203
7.201
7.126
7.121
7.048
7.004
6.999
6.998
Ph
Ph
Ph
Ph
N
H
3ka
0.98
2.06
2.01
2.12
0.94
3.96
1.91
4.65
3.10
2.89
0.67
1.00
3.00
1.00
f1 (ppm)


142.31
141.66
139.54
138.29
135.90
134.96
134.67
134.02
132.73
130.28
129.67
129.32
129.01
128.87
128.51
128.49
128.45
128.31
127.79
127.75
127.63
127.38
126.79
126.16
125.72
123.46
122.23
121.56
120.00
119.49
116.53
115.30
111.69
110.67
54.80
Ph
Ph
Ph
Ph
N
H
3ka
f1 (ppm)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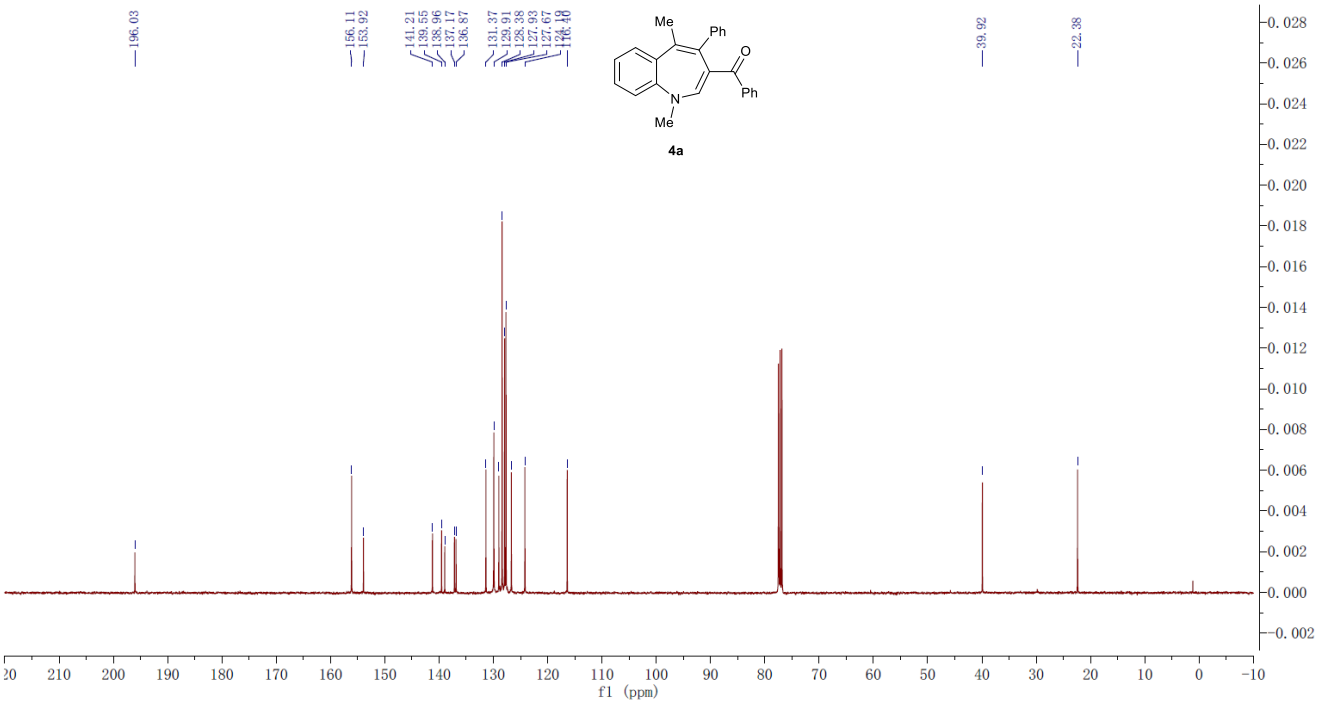
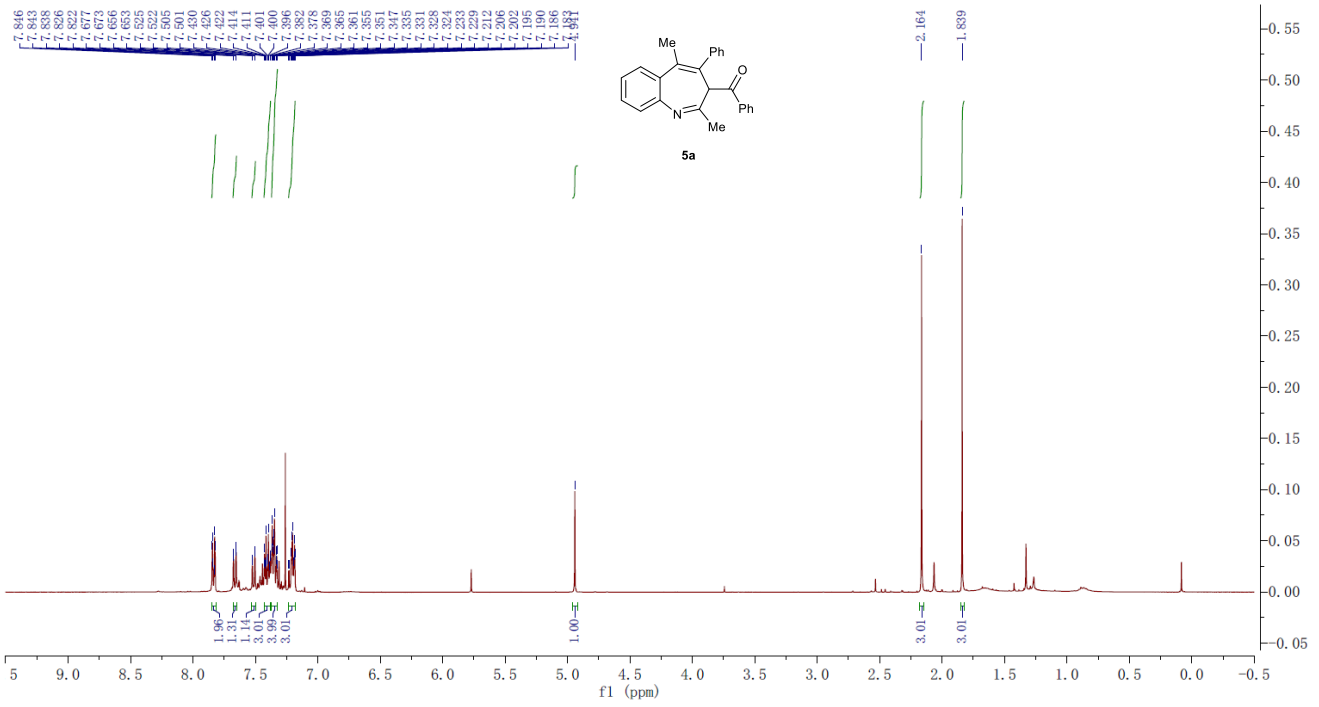
7.452
7.440
7.436
7.435
7.432
7.431
7.341
7.336
7.322
7.320
7.316
7.242
7.236
7.222
7.217
7.201
7.198
7.197
7.196
7.146
7.143
7.137
7.126
7.123
7.121
7.105
7.102
7.082
7.078
7.074
7.066
7.061
7.053
7.042
7.035
7.031
7.018
7.014
7.011
6.939
6.906
6.886
3.159
2.114
Me
Ph
O
Ph
N
Me
4a
1.96
1.89
2.94
3.01
0.93
2.01
1.00
1.00
3.01
3.01
f1 (ppm)


196.03
156.11
153.92
141.21
139.55
138.96
137.17
136.87
131.37
129.91
128.38
127.93
127.67
39.92
22.38
Me
Ph
O
Ph
N
Me
4a
f1 (ppm)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7.822
7.677
7.673
7.656
7.653
7.525
7.522
7.505
7.501
7.430
7.426
7.422
7.414
7.411
7.401
7.400
7.396
7.382
7.378
7.369
7.365
7.361
7.355
7.351
7.347
7.335
7.331
7.328
7.324
7.233
7.229
7.212
7.206
7.202
7.195
7.190
7.186
7.183
7.041
7.037
2.164
1.839
Me
Ph
O
Ph
N
Me
5a
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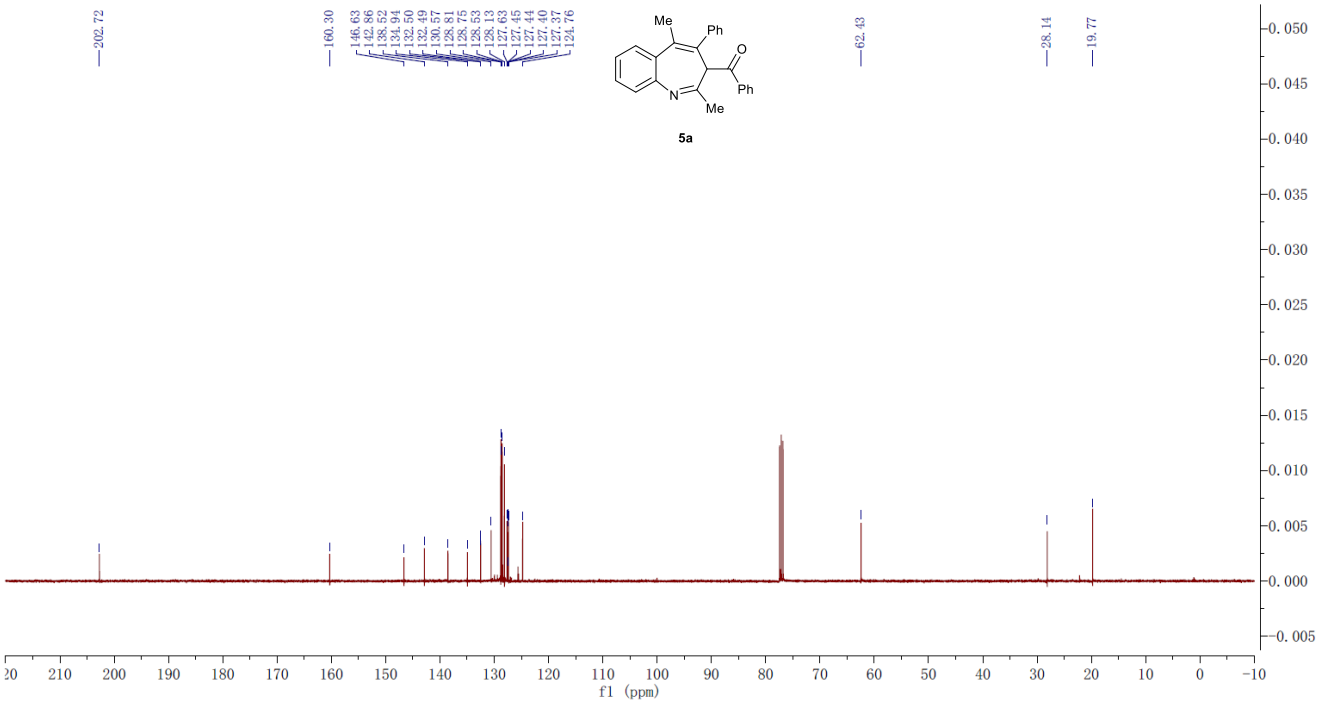
1.31
1.31
1.01
3.99
3.01
1.00
3.01
3.01
f1 (ppm)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146.63
142.86
138.52
134.94
132.50
132.49
130.57
128.81
128.75
128.53
128.13
127.63
127.45
127.44
127.40
127.37
124.76
62.43
28.14
19.77
Me
Ph
O
Ph
N
Me
5a
f1 (ppm)